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I.

CONTRIBUTION FROM THE CHEMICAL LABORATORY OF CASE SCHOOL OF APPLIED SCIENCE.

XX.—ON THE COMPOSITION OF THE OHIO AND CANADIAN SULPHUR PETROLEUMS.

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Presented October 10, 1894.

NOTWITHSTANDING the great number of investigations that have been undertaken on petroleums from different countries, our knowledge of their composition, especially of the portions with high boiling points, is still incomplete. What is known concerning American petroleums is based chiefly on the results of investigations which were carried on thirty years ago, before the discovery of several series of organic compounds, since shown to be contained in certain petroleums. With these facts in view, and having found in the study of the sulphur compounds from Ohio and Canadian petroleums that these oils are in certain respects peculiar in their composition, I have undertaken a comprehensive examination of them with reference to the different series of products which they may be found to contain. The study of Ohio petroleum seemed especially inviting on account of its origin in the Trenton limestone, a new horizon for a prolific oil supply, and its associations with animal remains in the oldest geological forma-

tions of the continent. A similar interest attaches to the Canadian petroleum from the Corniferous limestone, which has yielded since 1862 enormous quantities of oil within the limited areas, less than thirty square miles, at Petrolia and Oil Springs. From the information already acquired concerning the nature of the sulphur petroleums, they seem to possess, beside their distinctive characteristics due to sulphur constituents, qualities of other petroleums which differ essentially in their composition.

In the earlier attempts to ascertain the constituents of petroleum, the methods then employed for fractional distillation were so inadequate that very little was accomplished. In 1862 the first systematic examination of American petroleum was undertaken by Pelouze and Cahours,* who showed the presence of the series of hydrocarbons C_nH_{2n+2}, beginning with butane. On account of a want of suitable apparatus for fractional distillation, their results lacked precision, and the questionable assumption was based upon them that petroleum is composed principally, including the heavier oils and paraffine, of the homologues of marsh gas. In accordance with the suggestion of Watts, these bodies were called the paraffine hydrocarbons, and as such they have since been known in chemical literature. Having obtained from coal oil a series of hydrocarbons corresponding to certain members of the series discovered by Pelouze and Cahours, Schorlemmer † submitted the more volatile portions of American petroleum to distillation, and succeeded in separating hydrocarbons that had not been recognized by Pelouze and Cahours. In a more thorough and carefully conducted examination of Pennsylvania petroleum, carried on contemporaneously with the investigations of the chemists mentioned above, by means of an efficient fractional condenser devised especially for this and other similar investigations, C. M. Warren ‡ avoided the errors of other experimenters and established beyond question the presence in Pennsylvania oil of two series of hydrocarbons, each with an homologous difference in boiling points for CH_2 of 30°, and each member of one series differing in boiling point from the isomeric member of the other series by a little less than 8°. One of the series C_nH_{2n+2} identified by Warrren terminates at 127°.6, the other at 150°, the fractions of higher boiling points containing members of the series C_nH_{2n}. The assumption of Pelouze and Cahours that the frac-

* Comptes Rendus, LIV. 1241, LVI. 505, LVII. 62.

† Journ. Chem. Soc., 1862, p. 419.

‡ Mem. Amer. Acad. (N. S.), IX. 135; Proc. Amer. Acad., XXVII. 56.

tions with higher boiling points have the composition represented by the general formula C_nH_{2n+2} was shown to be erroneous by the results of Warren, which excluded members of this series above 151°.

The presence of aromatic hydrocarbons in American petroleum was first recognized by Schorlemmer in 1865. Pelouze and Cahours had previously stated that American petroleum contained no aromatic hydrocarbons, but Schorlemmer collected a distillate from Canadian petroleum below 150°, and upon treating it with nitric acid and reducing with tin and hydrochloric acid, after distillation he obtained an oil with an odor of aniline that gave, with bleaching powder, the rosaniline reaction. The portion distilling between 150° and 170° gave a mixture of solid and liquid nitro-products, and the solid portion proved to be trinitrocumol. Benzol and its homologues were also found by Schorlemmer in Pennsylvania petroleum, in Galician petroleum by Freund * and others, and in Hanover petroleum by Bussenius and Einstuck.† In Galician petroleum Pawlewski ‡ found two per cent of aromatic hydrocarbons, chiefly benzol and paraxylol, the latter never having previously been recognized in any petroleum. In the fraction 170°–190° from American kerosene, Engler § discovered pseudocumol and mesitylene by the formation of nitro-compounds, and calculating the weight of crude oil corresponding to the weight of kerosene taken, it was estimated that these constituents are contained in crude Pennsylvania oil to the extent of 0.2 per cent. These hydrocarbons were also found in German, Galician, Italian, and Russian petroleum, in the latter to the extent of 0.1 per cent. According to the results of Beilstein and Kurbatoff, ‖ the petroleum of the Central Caucasus has an essentially different composition from that of the deposits on the coast of the Caspian Sea. Oil obtained from the region of Zarskige Kolodzy, in the precinct of Tiflis in the Central Caucasus, proved to contain small amounts of benzol and toluol, but to consist principally, like the Pennsylvania petroleum, of the series C_nH_{2n+2}. Pentane, hexane, and heptane were identified. The oil from Baku on the coast contains the series C_nH_{2n+2} in smaller quantity, and Beilstein and Kurbatoff found no trace of the aromatic hydrocarbons C_nH_{2n-6}, but the principal constituents are members of the series C_nH_{2n}.

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* Ann Chem. Pharm., CXV. 19. † Ibid., CXIII. 151.

‡ Ber. der deutsch. chem. Gesellsch., 1885, p. 1915.

§ Ibid., 1885, p. 2234.

‖ Ibid., 1880, p. 1818; 1881, p. 1620.

In Pennsylvania petroleum, Beilstein and Kurbatoff * recognized hexahydroisoxylol. In the fraction 95°–100° the same chemists detected the presence of a body containing less hydrogen than is required for the series C_nH_{2n+2}. Crude American heptane, when treated with nitric acid, gave a nitro-product corresponding to the formula $C_7H_{15}NO_2$. Nearly coincident with the researches of Beilstein and Kurbatoff, Schutzenberger and Jonine † identified, in the petroleum of Baku, hexahydrobenzol and hexahydrotoluol.

In their classic researches on the composition of the Caucasus petroleum, Markownikoff and Ogloblin ‡ showed the presence, in the oil from Baku, of benzol, toluol, isoxylol, pseudocumol, mesitylene, isodurol, durol, and higher hydrocarbons of the composition $C_{11}H_{14}$, $C_{12}H_{14}$, $C_{11}H_{12}$, and $C_{13}H_{14}$, and others, possibly homologues of styrol and phenylacetylene. Contrary to the experience of others, Markownikoff and Ogloblin found the naphtha from the Balachani plain on the Apscheron peninsula very rich in aromatic hydrocarbons; in the oil from the Central Caucasus, naphtenes were found to the extent of 80 per cent, and the aromatic hydrocarbons C_nH_{2n-6} to the extent of 10 per cent. At first Markownikoff looked upon the naphtenes as isomeric with the hexahydro compounds, but later Markownikoff and Spady § appear to accept the identity of octonaphtene and hexahydroisoxylol. || As members of the naphtene series C_nH_{2n}, Markownikoff and Ogloblin identified hexahydromesitylene and the higher homologues between C_9H_{18} and $C_{15}H_{30}$. In petroleum from Boryslaw in Galicia, beside benzol, toluol, isoxylol, and mesitylene, Lachowicz ¶ found of the hexahydro series only hexahydroisoxylol.

The presence of unsaturated hydrocarbons C_nH_{2n} in American petroleum was not mentioned in the early publications of Pelouze and Cahours, nor were they referred to by Schorlemmer. Warren ** separated from Pennsylvania petroleum, rutylene, $C_{10}H_{20}$, boiling point 174°.9, margarylene, $C_{11}H_{22}$, boiling point 195°.8, and laurylene,

* Ber. der deutsch. chem. Gesellsch., 1880, p. 2028.

† Comptes Rendus, XCI. 823.

‡ Ann. Chim. Phys., [6], II. 372.

§ Ber. der deutstch. chem. Gesellsch., 1887, p. 1850.

|| In the Berichte, No. 7, April, 1895, recently received, the synthesis of 1–3-dimethyl hexamethylen, $C_6H_{10}(CH_3)$, is described by Zelinsky, and it is shown to be identical with the octonaphtene of Markownikoff, or hexahydroisoxylol.

¶ Ann. Chem Pharm., CCXX. 187.

** These Proceedings, XXVII. 56. Communicated May 12, 1868.

$C_{12}H_{24}$, boiling point 216°.2. In an examination of a hydrocarbon naphtha obtained as a product of the destructive distillation of a lime soap prepared from menhaden oil, Warren and Storer * discovered the series C_nH_{2n+2}, beginning with C_5H_{12}, members of the aromatic series including benzol, toluol, xylol, and isocumol, and a series of the general formula C_nH_{2n} as follows: rutylene, $C_{10}H_{20}$, margarylene, $C_{11}H_{22}$, laurylene, $C_{12}H_{24}$, identical with the hydrocarbons previously separated by Warren from Pennsylvania petroleum. Warren and Storer also submitted Rangoon petroleum to prolonged distillation, and they succeeded in proving the presence in this oil of rutylene, margarylene, laurylene, cocinylene, and naphthalene.

As early as 1842, Pelletier and Walther separated a hydrocarbon from the "steinöl" of Amiano boiling at 80°–88°, to which they assigned the formula C_7H_{14}. A similar product with the properties of heptylene was obtained by Mabery and Smith † as one of the products in the sulphuric acid extract from the refining of Ohio burning oil distillate.

More recently Engler ‡ subjected menhaden oil to distillation under a pressure of ten atmospheres, and from the distillates thus obtained hydrocarbons were separated which proved to be identical with those contained in natural petroleum. These products included the light constituents of gasoline, the hydrocarbons of which burning oil is composed, the heavy oils, and paraffine. Engler, therefore, believes in the origin of petroleum from the decomposition of animal remains. The hydrocarbons distilling above 160°, referred by Pelouze and Cahours to the series C_nH_{2n+2} may really be naphtenes or similar bodies. In most petroleums more recently examined, it is believed that the unsaturated hydrocarbons are not present in the crude oil, but when found in the products of distillation have resulted from decomposition. Beilstein and Kurbatoff stated that the series C_nH_{2n} in the Caucasus petroleum does not consist of the homologues of ethylene. In the lower fractions of Galician oil, Lachowicz obtained no reaction with bromine even after long standing. Above 200° the ready absorption of bromine indicated the presence of unsaturated hydrocarbons; but it was attributed to decomposition. On the other hand, Engler § found that petroleums from Alsace (Pechelbronn), Oelheim (Hanover),

* Mem. Amer. Acad. (N. S.), IX. 177.

† These Proceedings, XXV. 222.

‡ Ber. der deutsch. chem. Gesellsch., 1888, p. 1816.

§ Zeit. Ang. Chem., 1888, p. 73.

Tegernsee, Pennsylvania, Galicia, and Baku contain members of the series C_nH_{2n+2} and C_nH_{2n}, both unsaturated hydrocarbons and naphtenes. Engler asserts that all petroleums have the same composition, differing only in the proportions of their constituents. Markownikoff and Ogloblin * suggest the presence of unsaturated aromatic hydrocarbons in the oil from Baku.

Most analyses of crude petroleum have fallen short of 100 per cent, and the deficiency has been attributed to the presence of oxygen. In ascertaining the composition of oils from different districts, St. Claire Deville † showed that the percentage of oxygen varies between 2.1 per cent in the Canadian petroleum and 5.6 per cent in the oil from Zante. In 1874 Hell and Medinger ‡ attempted to separate acids from crude petroleum by agitating it with a solution of sodic hydrate and precipitating with sulphuric acid. The oil which separated was distilled and converted into a methyl ether. By saponification of this ether an acid was obtained to which was assigned provisionally the formula $C_{11}H_{20}O_2$. From the sodic hydrate solution used in the refining of Baku oil, by the addition of sulphuric acid, Aschan § separated a mixture of acids, and, taking advantage of a difference in solubility of their salts, he obtained one acid, $C_8H_{14}O_2$, distilling at 237°–239°, and another, $C_9H_{16}O_2$, that distilled at 251°–253°. The first acid, called by Aschan octonaphtenecarboxylic acid, by distillation with hydriodic acid, was converted into hexahydroisoxylol.

The oxygen compounds in petroleum were considered by Zaloziecki ‖ to be lacto-alcohols which are oxidized to acids by contact with air. By the same method which was followed by Heil and Medinger, and Aschan, Zaloziecki obtained an acid, $C_{10}H_{18}O_2$, to which he gave the formula,

$$\begin{array}{l} CH_2 \diagdown \\ \qquad\quad CH - (CH_2)_4 - CH \\ CH_2 \diagup \end{array} \begin{array}{c} \diagup CH_2 \diagdown \\ \\ \diagdown\ O\ \diagup \end{array} CHOH,$$

and to the hydrocarbon obtained by distillation with hydriodic acid he gave the formula,

$$\begin{array}{l} CH_2 \diagdown \\ \qquad\quad CH - (CH_2)_4 - CH \\ CH_2 \diagup \end{array} \begin{array}{l} \diagup CH \\ \quad \| \\ \diagdown CH. \end{array}$$

* Ber. der deutsch. chem. Gesellsch., 1883, p. 1873.

† Comptes Rendus, LXVI. 442; LXVIII. 485.

‡ Ber. der deutsch. chem. Gesellsch., 1874, p. 1216.

§ Ibid., 1890, p. 867; 1891, pp. 1864, 2710; 1892, p. 3661.

‖ Ibid., 1891, pp. 796, 1808.

Engler looks upon these acids as formed by oxidation of other constituents of the crude oil. According to the results of Markownikoff and Ogloblin,* the fraction 75°–85° from Caucasus oil contains 0.76 per cent of oxygen compounds, and the fraction 220°–230°, 5.21 per cent. These oxygen compounds are in part acid, in part neutral, and in part phenol. The acids $C_{10}H_{19}COOH$ and $C_{11}H_{21}COOH$ were obtained as colorless oils ; † Markownikoff and Ogloblin regarded these substances as naphtene carboxylic acids.

Most petroleums have been shown by analysis to contain nitrogen, usually in minute quantities. In distillates from Pennsylvania oil, Beilby ‡ found 0.08 per cent in the residuum or tar, and 0.375 per cent in the coke. Since the tar was one tenth of the crude oil, the latter contained 0.008 per cent of nitrogen. In crude Russian oil Beilby found 0.05 per cent. Peckham § found in West Virginia oil 0.54 per cent, in Mecca oil, 0.23 per cent, and in California oil, 0.56 – 1.1 per cent of nitrogen. In Egyptian oil, Kast and Kunkler ‖ reported 0.3 per cent of nitrogen, 1.21 per cent of sulphur, and 0.92 per cent of oxygen. Weller ¶ detected certain alkaloid bases in paraffine oil, and Bandrowski ** described a thick, transparent liquid solidifying at 20°, which he obtained by agitating Galician oil during several weeks with sulphuric acid. This substance gave a platinum salt containing 19.7 per cent of platinum. Upon neutralizing a sulphuric extract obtained in refining with calcic hydrate and distilling with steam, Zaloziecki †† obtained an oil containing nitrogen that formed a platosochloride whose percentage composition corresponded with that of tetrahydrocorridine $(C_{10}H_{19}NCl)_2PtCl_2$, or to the formula $(C_{10}H_{21}NCl)_2PtCl_2$; another insoluble platoso compound was shown by analysis to have the composition represented either by the formula $(C_{10}H_{15}NCl)_2PtCl_2$ or $(C_{10}H_{17}NCl)_2PtCl_2$.

Several hydrocarbons have been described as occurring in the less volatile portions of American petroleum. Hemilian ‡‡ obtained from the high boiling fractions "petrocene," a crystalline body melting

* Ann. Chim. Phys., [6.], II. 372.

† Ber. der deutsch. chem. Gesellsch., 1883, p. 1873.

‡ Journ. Soc. Chem. Ind., 1891, p. 120.

§ Geological Survey of California, Appendix to Vol. XL., p. 89.

‖ Chem. Centralb., 1890, p. 932.

¶ Ber. der deutsch. chem. Gesellsch , 1887, p. 2097.

** Monatsheft für Chem., VIII. 224.

†† Ibid., XIII. 498.

‡‡ Ber. der deutsch. chem. Gesellsch., 1876, p. 1604.

above 300°. To this substance was assigned the formula $C_{32}H_{22}$. Prunier and David * stated that they had obtained evidence of the presence in refinery residues of anthracene, chrysene, pyrene, phenanthrene, chrysogene, retene, benzerythrene, fluoanthrene, parachrysene, paraanthracene, an isomeric acenaphtylene, besides different paraffines and stilbene. In the "petrocene" and "carbopetrocene" prepared from the tarry residue of petroleum, Prunier and David identified compounds, the former melting at 160°–190°, the latter at 200°–238°, and also thallene melting at 110°. They attributed the green fluorescence in petroleum to the presence of chinones. Inasmuch as these products were obtained from the distillation of tar in coking, evidently no inference is permissible concerning their presence in the crude oil. From "petrocene," Sadtler and McCarter † separated two hydrocarbons, one of which melted at 280° and the other at 178°. From these hydrocarbons the chinones were prepared, and from one an alizarine.

In undertaking an examination of the Ohio and Canadian sulphur oils with the advantage of former experience in studying the sulphur constituents, it was evidently necessary to conduct the distillations with all possible precautions to avoid decomposition. The tendency of the sulphur oils to decomposition by heat is due as much at least to the action of air on the hot oil as to the increased temperature. Markownikoff and Ogloblin attributed the decomposition in the distillation of the Russian oil to polymerization of the unsaturated compounds, and perhaps also to the polymerization of certain aromatic compounds, such as phenylacetylene, and they found that coloration of distillates on standing was less marked when the oxygen compounds had been removed. This tendency towards polymerization in unsaturated hydrocarbons separated from sulphuric acid solutions was observed by me, ‡ and it will receive further attention. It was therefore deemed advisable to carry on all distillations from the crude oils, instead of relying upon refinery products, except only the most volatile distillates, and the advantage gained has been apparent in subsidiary distillations of refinery oils which had been subjected to the decomposition incident to refinery distillation. Longer time is then necessary for separations, and the odor of decomposition is retained indefinitely during subsequent distillations. Certain constituents of the sulphur petroleums are even more unstable than the sulphides, as

* Bull. Soc. Chim., [2.], XXXI. 158.
† Amer. Chem. Journ., 1879, p. 30.
‡ Ibid., 1893, p. 92.

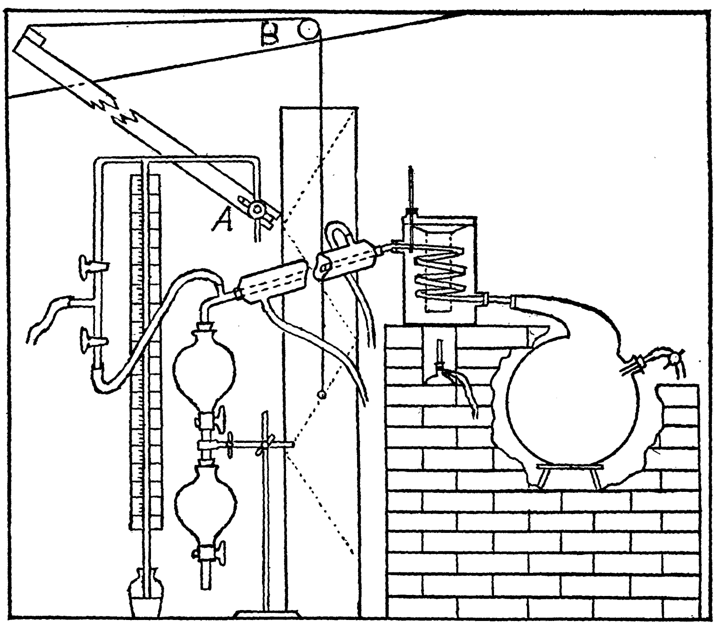
shown by the rapid coloration of the oils when distilled, even after removal of the sulphides by mercuric chloride. Nevertheless, in the separation of constituents requiring larger quantities of distillates than can conveniently be collected *in vacuo*, since only porcelain or earthen ware stills are admissible on account of the decomposition in metallic stills, it may be necessary to depend to a limited extent upon refinery distillates.

After the first distillation of the crude oils *in vacuo*, distillation of the portion collected below 150° was continued under atmospheric pressure, since it occasioned no appreciable decomposition. Under the diminished pressure some loss of the constituents with low boiling points could not be avoided; but this was not important, since refinery distillates could be utilized for the separation of the volatile hydrocarbons. Distillation of considerable quantities of oil *in vacuo* presented certain difficulties. Neither glass nor metallic stills were suitable, and no American earthen ware stills could be procured that would support a vacuum on account of porosity from imperfect moulding and glazing. Some of the English earthen ware has supported a vacuum, but the ideal stills for such work, or for any distillations in large quantities, when metals cannot be employed, are those manufactured in the Royal Berlin Porcelain Factory. We have had a three-gallon porcelain still and several others of smaller capacity in operation almost continuously during several months with apparently no deterioration. When these stills are enclosed within a brick chamber, the temperature of distillation may, without difficulty, be carried above 350° by means of large laboratory burners. Another serious obstacle immediately presented itself in the porosity of common corks, which alone could be used for connections. After much labor it was found that tight joints could be secured by means of a rubber lute made by dissolving gum rubber in very light gasoline. Thin films of this lute drawn by the inward pressure into the joints and imperfections in the corks, after several applications, formed sufficiently close connections. Any other than the lightest gasoline as a solvent leaves a sticky film that is unpleasant to manipulate.

An important feature in prolonged fractional distillations *in vacuo* is a simple and convenient means for maintaining, without too close attention, a constant tension within the still. Air must not come in contact with the hot oil or vapor, and it would require too large quantities of an inert gas. An expedient suggested itself in the fact that occasionally small leaks held the manometer column stationary at whatever height it happened to stand. It therefore seemed possible to

graduate leaks apart from the still in such a manner that the tension could be held constant for some time at any desired point.

The accompanying figure represents the form of regulator that has been used in all our distillations of large as well as small quantities of oils, together with the complete apparatus in the form for use. The regulator consists simply of a glass stopcock, A, better of considerable size, attached to the manometer by means of a side tube. To regulate closely the inflow of air an arm three to five feet in length,



according to the working of the stopcock, is attached firmly to the head of the cock, and supported in a manner easily movable within very small divisions on the arc of a circle of which it is the radius. To enable the operator to make adjustments while standing in front of the manometer, a piece of lead is attached as a weight to the upper end of the lever, and a cord is carried over a pulley, B, and terminates in a ring in front of transverse rows of pins a few millimeters apart. For economy of space the pulley is placed lower in the figure than its actual position. The upper part of the lever consists of two strips of wood, with a space between, through which passes a rigid copper wire as a support and guide. With the lever in a vertical position, the

stopcock is fully open; any adjustment is easily obtained, and the manometer may be held stationary within one millimeter at any desired point during several hours.

In the distillation of small quantities of liquids requiring constant attention, we have used a piece of glass tube forty-five to sixty millimeters long, attached to the side stopcock, with a sliding support near the end. In vacuum distillations on a large scale it is more convenient to refer to the entire length of the manometer column, since at any time leaks may occur that are indicated only on the lower portion of the graduated scale. With a short manometer column alone, much time may be lost in waiting for an exhaustion that is interfered with by leaks.

In heating the still, direct contact with the flame was prevented by maintaining an air space above the burner by means of a sheet of asbestos. With such application of heat equally on the sides and bottom, there was less danger of decomposition at high temperatures. All but the highest distillates were collected in a Warren hot condenser containing a glass worm. With this condenser vacuum distillations are easily controlled, and, as in distillations under atmospheric pressure, with a great economy in time. Continuous distillation is possible without losing the vacuum, by drawing in consecutive fractions through the rear tubulure of the retort. The two receivers shown in the figure are convenient, and some additional advantage would be gained by means of an independent vacuum connection with the lower receiver. Several supports are not represented in the figure. Much time and tedious labor were expended on this apparatus before all the difficulties were overcome; but the compensation was ample, since by means of it we have been able to separate in considerable quantities constituents of high boiling points without decomposition, which otherwise would have been impossible. As an evidence of its usefulness, during several months continuous distillations were in progress, in charge of assistants, with highly satisfactory results. Distillates were collected at intervals of 10°, 5°, and 2°. The depression in boiling points by the diminished pressure in vacuum distillation varies between 60° and 65° for the lower constituents, and 125° or more for those collected between 300° and 350°. The residue above 350° (450°–500° atmospheric pressure) in both Ohio and Canada oils had apparently undergone but little decomposition; in appearance, it was a thick, ready flowing oil, with scarcely any odor.

A portion of the residual oil above 350° *in vacuo* was redistilled in an ordinary boiling flask, and the temperatures of the vapor and of

the liquid were read on a Mahlke 550° thermometer. The oil began to distil with much decomposition at 385° in the vapor, and 415° in the liquid. One half distilled with the temperature in the liquid below 430°. Doubtless the temperatures of distillation were much reduced by the decomposition. Since we have found that distillations below 250° may be carried on successfully without serious decomposition in an atmosphere of carbonic dioxide, when we return to the distillation of the higher constituents this method may be serviceable.

Ohio Petroleum.

In the study of Ohio petroleum I have been aided by Mr. E. J. Hudson.* Besides the publications from this Laboratory on the sulphur compounds † and those of Orton, ‡ I am aware of no published statements concerning the composition of Ohio sulphur petroleum. The crude oil which formed the basis of our work was received from the Peerless Refining Company, Findlay, which controls a large section of oil territory. When received, it was of a somewhat thicker consistency than ordinary Pennsylvania oil, with a slight odor of hydric sulphide that is usually observed in crude sulphur oils. It contained a small quantity of water, which was removed completely only after long standing with fused calcic chloride. In determining the specific gravity of Ohio sulphur petroleums, oils were collected from wells at different points in the Findlay and Lima fields. The determinations were made at 20°.

Findlay Field.

		Specific Gravity.
(1)	Barnsville	0.8272
(2)	Heilstone Oil Co., Well No. 2, Hancock County	0.8296
(3)	Ohio Oil Co., Wood County	0.8194
(4)	Langmade Well, No. 4, Portage, Hancock County	0.8149
(5)	Peerless Refining Co., Well No. 2, Liberty, Hancock County	0.8278
(6)	Peerless Refining Co., Well No. 5, Baltimore, Wood County,	0.8239

* A part of this work formed the subject of a thesis by Mr. Hudson for the degree of Bachelor of Science

† These Proceedings, XXV. 218; Amer. Chem. Journ., XVI. 83.

‡ Ohio State Geological Reports, 1886, 1888, 1890; U. S. Geological Report, 1886–87.

LIMA FIELD.

The following specimens of crude oil, representing different portions of the Lima and Findlay fields, were received from the Ohio Oil Company, with a history of each well: —

	Township.	County.	Drilled.	Sand.	Oil.	Depth.	Production after shot.	Production at present.
				ft.	ft.	ft.	Daily.	Daily.
(1)	St. Mary's	Auglaize	May, 1892	1132	1147	1166	100 bbls.	5 bbls.
(2)	Liberty	Hancock	Aug., 1893	1250	1273	1286	75 "	10 "
(3)	Montgomery	Wood	Oct., 1892	1192	1197	1242	25 "	5 "
(4)	Woodville	Sandusky	July, 1892	1180	1195	1205	125 "	10 "
(5)	Nottingham	Wells, Ind.	April, 1895	990	1004	1044	165 "	75 "
(6)	Liberty	Wood	Sept., 1894	1152	1172	1227	125 "	30 "
(7)	Lima	Allen						

	(1)	(2)	(3)	(4)	(5)	(6)	(7)
Sp. gr.	0.8288	0.8345	0.8265	0.8254	0.8244	0.8428	0.851

There is evidently an appreciable variation in the composition and properties of the oils from different points in the Ohio field. Marked differences occur in the specific gravity as well as in the percentages of carbon, hydrogen, nitrogen, and sulphur.

The oil that was employed in this examination was somewhat heavier, with a specific gravity 0.8380. These results show an appreciable variation even in different portions of the same field. A similar variation in specific gravity has been observed in other fields: —

		Specific Gravity.
Alsace (Pechelbronn), depth 146 feet	(Engler)	0.906
" " " 213 "	"	0.885
Oelheim (Hanover)	"	0.889
Tagernsee	"	0.815
Pennsylvania	"	0.8185
"	"	0.801
Galicia	"	0.8235
Baku	"	0.859
"	"	0.810
Ohio	(Mabery)	0.838

		Specific Gravity.
Ohio	(Markownikoff and Ogloblin)	0.887
Baku (Apscheron)	" " "	0.855–0.885
Galicia	" " "	0.835–0.895
American Petroleum	(Petrolitz)	0.830
" "	(Weil)	0.827
Canada	(Markownikoff and Ogloblin)	0.828
"	" " "	0.844
Alsace (Pechelbronn)	" " "	0.668

The value 0.887 assigned by Markownikoff to Ohio oil is much higher than has elsewhere been given. It must have been obtained in an oil from another Ohio field, perhaps from the Mecca district. The values given by Markownikoff for Canada oil must refer to a product from the Oil Springs district, although the number 0.828 is lower than is usually found even in that oil. The numbers given by Redwood are 0.844–0.854 for Oil Springs oil, and 0.859–0.877 for Petrolia oil. In Oil Springs oil we found 0.8427–0.8389 (gas oil), 0.8442, and in Petrolia oil, 0.8553, 0.8621, 0.8800.

In ascertaining the quantity of sulphur by combustion in air in the crude oil from which distillates were prepared for examination, the following results were obtained: (1) 0.73 per cent, (2) 0.72 per cent, (3) 0.72 per cent. In oils previously examined the percentage of sulphur has not been above 0.60 per cent. Sulphur was also determined in the oils collected in the Findlay and Lima districts in the order of the numbers given above: —

	Findlay.	Lima and Findlay.		Findlay.	Lima and Findlay.
(1)	0.33	0.61	(5)	0.68	0.56
(2)	0.63	0.71	(6)	0.61	0.76
(3)	0.56	0.37	(7)		0.81
(4)	0.68	0.49			

In Apscheron oil, Markownikoff and Ogloblin * obtained 0.064 per cent, and 0.16 per cent in Trans-Caspian oil.

The percentages of carbon and hydrogen in the oil from which distillates were obtained were found by combustion in air with a layer of plumbic peroxide in front to retain the sulphur †: carbon, 84.57; hydrogen, 13.62. In other samples from Findlay and Lima carbon and hydrogen were also determined: —

* Ann. Chem. Phys., [6.], II. 393. † Warren, These Proceedings, VI. 472.

	Findlay.		Lima and Findlay.	
	C.	H.	C.	H.
(1)	85.76	13.56	84.73	13.48
(2)	85.82	13.80	84.03	13.05
(3)	84.33	13.46	83.89	13.18
(4)	84.35	13.36	84.55	13.55
(5)	84.20	13.41	83.41	13.13
(6)	84.18	14.60	85.07	13.33
(7)			85.00	13.05

The percentages of carbon and hydrogen that have been found in analyses of oils from other deposits are given in the following table: —

	O.	H.	O.
Apscheron (Markownikoff and Ogloblin)	86.65	13.35	
" " " " "	87.01	13.22	
" " " " "	86.89	13.18	
Trans-Caspian (Markownikoff and Ogloblin)	86.75	12.19	
Egyptian (Kast and Kunkler) *	85.85	11.72	
Pechelbronn (Sainte-Claire Deville) †	85.7	12.00	2.3
Galicia (Sainte-Claire Deville) †	82.2	12.10	5.7
Rangoon (Sainte-Claire Deville) †	83.8	12.7	3.5

The following values represent the percentages of carbon and hydrogen in crude petroleum from other American oil fields: —

	O.	H.	O.
W. Virginia, Scioto Well (Peckham) ‡	86.62	12.93	
W. Virginia Cumberland Well (Peckham) ‡		13.38	
California oil (Peckham) ‡		11.82	
Mecca oil (Peckham) ‡	86.32	13.07	
Canada, Manitoulin (Deville) †	83.00	14.6	2.4
Canada, Petrolia (Deville) †	84.5	13.5	2.0
Canada West (Deville) †	79.4	14.1	6.5
Ohio oil (Deville) †	84.2	13.1	2.7
Pennsylvania oil (Deville) †	83.4	14.7	1.9
Pennsylvania oil (Deville) †	84.19	13.7	1.4

* Chem. Centralb., 1890, p. 932.
† Comptes Rendus, LXVIII. 485.
‡ Geological Survey of California, Vol. XI., Appendix, p. 39.

In the crude oil used in this examination, and in the other specimens described above, nitrogen was determined by the Kjeldahl method, and several closely concordant results were obtained by combustion with soda lime; the former gave 0.11 per cent, and the other oils the following percentages: —

	Findlay.	Lima and Findlay.
(1)	0.26 per cent	0.068
(2)	(*a*) 0.023, (*b*) 0.023 per cent	0.047
(3)	0.21 per cent	0.054
(4)	0.13 "	0.049
(5)	0.35 "	0.060
(6)	0.08 "	0.056
(7)		0.024

The presence of nitrogen in Ohio and Canadian petroleum will receive further attention at the close of this paper in some observations on the origin of petroleum.

The bromine absorption in the crude oils was determined by the method described in Allen's Commercial Organic Analysis. A weighed quantity of the oil was allowed to stand in the dark with a slight excess of bromine dissolved in dry carbonic disulphide, and the portion not absorbed was titrated with standard solutions of sodic hyposulphite and iodine. The strength of the bromine solution was ascertained by parallel titrations. Approximately one per cent of hydrobromic acid is evolved in these determinations in crude oils.

	Findlay.	Lima and Findlay.		Findlay.	Lima and Findlay.
(1)	11.29	8.74	(5)	13.07	10.93
(2)	14.62	9.31	(6)	11.32	12.31
(3)	10.55	11.49	(7)		12.06
(4)	14.89	12.30			

A comparison of the bromine absorption of the sulphur oils with that of oils from other sources indicates that bromine absorption is independent of sulphur compounds, and a distinctive property of petroleums in general. The following determinations were made: —

Chinese petroleum	10.90 per cent
Italian petroleum	7.10 "
Macksburg, O., petroleum	9.74 "
Berea Grit, O., petroleum	10.71 "
California petroleum	9.88 "

The quantities of bromine absorbed by distillates from the crude sulphur oil were also determined: —

Fraction.	Percentage of Bromine absorbed.
110°–150°	0.73
150°–220°	1.74
220°–257°	4.84
257°–300°	5.04
300°–330°	12.10
Residue	19.50

Throughout this investigation some reliance has been placed on the absorptive capacity for bromine of crude oils and distillates obtained from them as indicating a certain unsaturated condition. While it should be borne in mind that a considerable proportion of the bromine absorption is due to the sulphur constituents, there is besides a large absorption in the crude oils and in the residues of distillation above 350° by other constituents. There is much yet to be learned concerning the decompositions in distillations at high temperatures, which are indicated by the greatly increased bromine absorption, and the study of the higher boiling portions will be greatly facilitated by the aid of the Mahlke thermometers for observing temperatures below 550°.

The characteristic qualities of Ohio oil appear also in the proportions that distil at different temperatures; 800 grams of the crude oil collected in the following proportions beginning at 110°: —

	110°–150°	150°–220°	220°–257°	257°–300°	300°–350°	Residue.
Grams	76	133	86	76	69	348
Per cent	9.75	16.63	10.75	9.75	8.63	43.5
Sp. Gr. at 20°	0.7282	0.7669	0.7940	0.8138	0.8242	0.8976
Per cent sulphur	0.10	0.38	0.41	0.37	0.37	0.54

The distillates below 225° were colorless, and no odors resulting from decomposition were observed. Above this point color appeared in the distillates, with the odor of decomposition, which became more marked with increasing temperatures. Above 275° the heavier paraffine oils began to distil. In refinery distillation of Ohio petroleum it is therefore evident that cracking begins in the vicinity of 250°. No doubt crude sulphur petroleums undergo decomposition spontaneously to some extent, since upon standing they always contain hydric sulphide. We find that certain unstable constituents separated from the crude oils gradually become darker in color, with other indications of chemical change. At the beginning of the distil-

lation hydric sulphide came off in considerable quantities, but after the first fraction very little appeared in the succeeding distillates below the point where decomposition began.

On account of the viscous character of the Ohio and Canadian petroleums, and the large proportion of heavy oils, temperatures indicated by the thermometer in the vapor of the distillates should he higher than the corresponding temperatures of the oil. To ascertain this difference, crude Findlay oil was distilled, and the temperatures of the distillates and of the oil were noted with the following results: —

Thermometer in the Oil.	Thermometer in the Vapor.	Difference.
°	°	°
167	120	47
180	140	40
203	160	43
221	180	41
238	200	38
259	220	39
282	240	42
301	260	41
318	280	38
341	300	41

Except in the first reading the average difference in temperature is about 40°.

Determinations of sulphur in the crude oil and in the distillates obtained from it, showed that considerable sulphur was lost during distillation. In order to obtain definite information concerning the quantity lost, 100 grams of the crude oil were distilled under atmospheric pressure, and attached to the receiver were flasks containing a solution of sodic hydrate for the purpose of absorbing any hydric sulphide that escaped. In front of the flask containing hydric sulphide there was connected another flask, which contained alcohol, with a delivery tube in front to absorb volatile products that might result from decomposition. The oil was fractioned to 300°, collecting between 115° and 250°, and between 250° and 300°, and the hydric sulphide was determined after oxidation with bromine by precipitation with baric chloride. The percentage of sulphur in the several fractions was also determined. As usual in distillation of the sulphur petroleums, a slight sublimate of sulphur was observed in the neck of the condenser. Upon diluting the alcohol it became slightly turbid, which indicated probably some volatilization of sulphur constituents.

The alkaline solution of the sulphur from the distillate 115°–250° gave 0.1135 gram of baric sulphate, corresponding to 0.0156 gram of sulphur. From the alkaline solution of the sulphur absorbed from the fraction 250°–300°, 0.6946 gram of baric sulphate was obtained, corresponding to 0.0958 gram of sulphur. A determination of sulphur in the distillate 115°–250° gave 0.55 per cent; in the distillate 250°–300°, 0.51 per cent; and in the residue above 300°, 0.60 per cent. Since the weight of the distillate collected at 115°–250° was 20.55 grams, the weight at 250°–300°, 5.1 grams, and the weight of the residue above 300°, 74.35 grams, the total weight of sulphur accounted for in these determinations was 0.7166 gram, leaving 0.27 gram which must have escaped in ways not determined.

In comparing the quantities of the distillates from Ohio oil, and their specific gravities, with those obtained by Markownikoff and Ogloblin * in the Apcheron oil with a specific gravity at 17° of 0.882, and those given by Bolley from Pennsylvania petroleum with a specific gravity of 0.816, it is evident that the properties of Ohio petroleum place it between the Caucasus and Pennsylvania oils.

The Caucasus oil began to distil at 120° in the vapor, and 180° in the liquid.

	Apscheron.		Pennsylvania.			Ohio.	
°	Parts in 100.	Sp. Gr.	Parts in 100.	Sp. Gr.	°	Parts in 100.	Sp. Gr.
120–150	0.5	0.786	19.70		110–150	9.75	0.7282
150–200	10.9	0.824	8.85	0.757	150–220	16.63	0.7669
200–250	12.8	0.861	15.23	0.788	220–257	10.75	0.7940
250–320	24.7		20.7	0.809	257–300	9.75	0.8138
					300–350	8.63	0.8242
Total	47.9		64.48			55.51	
Residue	53.1		35.52			43.00	

While the temperatures at which the Ohio oil was collected are slightly different from the others, they are sufficiently close for comparison.

Kramer † has compared the quantities of distillates obtained from crude petroleum of other fields: —

	Sp. Gr.	—150°	150°-250°	250°-300°	Residue.
Tagernsee	0.812	20.04	26.12	14.00	35.91
Pennsylvania	0.814	14.34	25.35	13.75	40.99
Baku	0.880	0.63	12.73	15.55	37.95
Oelheim	0.885	0.74	11.05	9.75	75.71
Alsace	0.888	1.3	16.37	17.07	47.88

* Ber. der deutsch. chem. Gesellsch, 1883, p. 1873.

† Chem. Centralb., 1887, p. 290.

Taubes Barlâdu* distilled 1115 c.c. of crude Roumanian petroleum from the deposits on the south slope of the Carpathians, which are probably connected with the Galician oil zone, with the following results:—

°	c.c.	Per cent by Volume.
30–125	150	13.5
125–225	385	35.5
225–280	160	14.3
280–315	98	8.1

In an examination of Burmese petroleum, Romanis † obtained an oil from Yay-nan-Chaung with a specific gravity of 0.8590, which solidified at 24°. An oil from Arracan with a specific gravity of 0.825 at 32° contained considerable benzol and other aromatic hydrocarbons; upon distillation, the following results were obtained:—

	Per cent.
70–90	3.1
90–100	7.6
100–130	10.6
130–200	18.7
200–300	18.7
+ 300	12.5
Oil in residue	8.0
Paraffine	3.1
Loss	17.7
	100.00

Distilled with Steam.

°	Per cent.
—100	23.3
100–110	33.0
110–130	29.3
Residue	13.3 (heavy oil)
	98.9

Markownikoff and Ogloblin examined the ash of Caucasus petroleum by igniting the residue of distillation. They found 0.09 per cent of ash calculated for the original quantity of crude oil, and it consisted chiefly of the oxides of calcium, iron, and aluminum. Traces of copper and silver were also found. We have determined by combustion in oxygen the percentages of carbon and hydrogen in coke from the refinery residue of the distillation of Ohio petroleum; the per cent of carbon was 95.06, and that of hydrogen 4.85. A determination of nitrogen by the Kjeldahl method gave 0.31 per cent. The quantity of ash in the coke was determined by burning off the carbon, and the weight of ash thus obtained corresponded to 0.11 per cent of the coke burned. In attempting to estimate the percentage of ash in the crude

* Zeit. Ang. Chem., 1889, p. 606.

† Chem. News, LIX. 292.

oil from the amount found in the coke, there is some uncertainty as to the quantity of oil corresponding to the coke. In some oils the proportion of residue is estimated as ten per cent of the crude oil. It depends also upon the method followed by the refiner. Sometimes the first distillation of the crude oil is pushed to the point of complete decomposition, and the tar distillate is again distilled until it is coked. It is well known that earthy matter frequently remains for some time in suspension in the crude oil after it is taken from the wells. On this account, if the oil was distilled before the suspended material had subsided, the ash would not represent what had been in solution in the oil. But the oil is usually allowed to stand some time before distillation, and that the coke we examined was practically free from suspended matter is evident from the low percentage of ash, and corresponding results with Canadian oil where the ash was determined in a tar distillate and in coke from crude oil; the percentages of ash from the two sources were not very different.*

In Findlay oil, in which our determination was made, the proportion of still residue is doubtless somewhat smaller than that mentioned above, probably between ten and five per cent. The corresponding percentage of ash in the crude oil would, therefore, be not far from 0.005 per cent, an amount considerably less than Markownikoff and Ogloblin found in Russian oil.

An analysis of the ash showed that it was composed chiefly of lime and magnesia, and the quantity of magnesia is at least equal to that of the lime. Traces of iron and aluminum were found, the iron possibly having been dissolved from the still. It is therefore evident that the crude oil has exerted an appreciable solvent action on the limestone reservoir, dissolving both constituents of the dolomitic rock.

It is maintained by some chemists that all petroleums contain the same series of compounds in different proportions, and that the difference in properties depends upon a variation in the quantities of the constituents. In a general sense, with respect to the principal series of hydrocarbons this is doubtless true; yet there is such a wide difference in the properties of oils like those from Pennsylvania and the Caucasus that they are characteristic of substances quite unlike. The Caucasus petroleum is wholly, or nearly, wanting in the series C_nH_{2n+2}, and the Pennsylvania oil evidently contains the series C_nH_{2n} in much smaller proportion than the Russian oil. The presence of the higher members of the latter series in the Pennsyl-

* Determination of Ash in Canadian Petroleum, page 51.

vania oil has yet to be ascertained. It is conceivable that the difference in the composition of petroleums is due to the different influences to which they have been exposed. Perhaps greater porosity of the reservoir or cover where oils exist under pressure has permitted an escape from certain oils of the more volatile constituents, especially of the series C_nH_{2n+2}. If this should be demonstrated by more extended observations, it would be reasonable to expect the same bodies in the Pennsylvania as in the Russian oil, only in smaller quantities of the higher constituents. Referring the sulphur in Ohio petroleum to the average composition of the compounds containing it, the crude oil should contain at least five per cent of the sulphur derivatives. Evidently such a large proportion of sulphur compounds in petroleum must exert an important influence on its properties, and we should therefore expect a marked difference between the sulphur petroleums and those which contain only traces of sulphur.

From a general similarity of Ohio petroleum to the oil from Pennsylvania, so far as it relates to hydrocarbons of the series C_nH_{2n+2}, it should perhaps be expected that the composition of the latter oil, which has been established beyond question, at least so far as the portions of low boiling points are concerned, should represent also similar portions of the Ohio product. As mentioned above, even a casual examination of the sulphur oils affords abundant evidence that their peculiar properties depend upon other constituents than the hydrocarbons C_nH_{2n+2}. While these unique constituents may detract from, rather than enhance, the value of the sulphur oils for commercial purposes, it is as important for the intelligent guidance of the refiner as it is interesting from a scientific point of view that they be well understood.

While occupied with the sulphur compounds in Ohio petroleum, I was impressed with the complexity in composition manifested by the products of distillation, and with the importance of a thorough examination for all constituents. We therefore began with an endeavor to separate and identify the individual homologues of methane which have been found in Pennsylvania petroleum, including an approximate quantitative determination of all but the more volatile members.

HYDROCARBONS C_nH_{2n+2}.

To separate the hydrocarbons of lower boiling points we obtained twenty-five litres of the very first distillate from a three-hundred barrel still. This distillate contained 0.10 per cent of sulphur.

Considerable gas always escapes in refinery distillation before a liquid distillate appears, but we have not yet undertaken an examination of its composition. Probably this is essentially the same as that of the gas given off in beginning a distillation of Pennsylvania oil together with hydric sulphide, which is always evolved to a greater or less extent in the distillation of sulphur petroleums. Sadtler * found that the gas from Pennsylvania wells consisted principally of methane, with some ethane, nitrogen, and hydrogen. In the gas from Canada wells, at Enniskillen, Fouqué † found marsh gas, ethane, and small quantities of carbonic dioxide. According to Ronalds, ‡ the gas from Pennsylvania petroleum contains 1.27 per cent of carbonic dioxide, 6.58 per cent of oxygen, 54.00 per cent of nitrogen, and 38.15 per cent of ethane and propane; by exposing the escaping gas to a freezing mixture, butane was condensed to a liquid.

In an exhaustive study of natural gas from Pennsylvania wells, Phillips § found that the principal constituents were hydrocarbons C_nH_{2n+2}, with nitrogen in variable proportions and carbonic dioxide in small quantity, but no hydrogen nor carbonic oxide.

The crude distillate was subjected to fractional distillation in a porcelain still, to which was attached a Warren condenser filled with a mixture of salt and ice, with ice alone, or with water, according to the fraction collected. Another ordinary condensing worm surrounded with a freezing mixture was placed in front. Subsequent distillations were conducted in glass stills, and the fractions rapidly accumulated within limits of temperature which distinguish the hydrocarbons C_nH_{2n+2}. At the beginning of the first and second distillations, a delivery tube was attached to the bottle receiving the distillate, and extended so as to collect in a receiver inverted over water any volatile constituents that might have escaped condensation. At first a very little gas collected, which burned with a smoky flame, but none afterwards. The following quantities were collected during the first distillation: —

	−25°	25°–30°	30°–35°	35°–40°
Grams	525	400	450	400

After the fourth distillation thirty-five grams collected between 0° and 1°, distilling for the most part at 0°, barometer 740 mm. This was evidently butane, boiling point 0°. Inasmuch as the boiling point of

* Amer. Chemist, 1876, p. 97.
† Comptes Rendus, LXVII. 1045.
‡ Journ. Chem. Soc., XVIII. 54.
§ Amer. Chem. Journ., 1894, p. 406.

this hydrocarbon has been carefully determined,* further examination was not deemed necessary. The temperature rose rapidly to 5°, and between 7° and 9° 20 grams of a distillate collected, mostly between 7° and 8°, the boiling point of a hydrocarbon which was separated by Warren from Pennsylvania petroleum, and which was regarded by him as one of the butanes. Since the atmospheric temperature was in the vicinity of 30° when these distillations were in progress, special care was necessary to preserve the distillates, and the ice accidentally becoming exhausted in the ice-chest, the distillate collected at 0° burst the bottle, and the one at 8° forced out the stopper and volatilized. Of the two possible butanes, the boiling point of one is without question 0°. The other seems to have been obtained by Butlerow † from isobutyl alcohol, and the boiling point assigned to it was —17°.5. Under more favorable conditions, we shall collect a larger quantity of this distillate, to determine by its chemical behavior, as well as by its constancy in boiling point, whether it be a definite compound.‡

Considerable quantities of distillates collected below 30°, but by continued distillation they were mostly separated into higher and lower constituents, indicating the absence of individual products. In the vicinity of 30° the fractions were large, amounting to 300 grams between 28° and 32°. After the ninth distillation, 75 grams collected between 29° and 30°, with the barometer at 747 mm. A vapor density determination gave 2.52, required for pentane 2.49. This product was, therefore, isopentane, boiling point 30°. Between 36° and 37°, 75 grams distilled, and this distillate was shown by its vapor density to have the composition required for pentane; a vapor density determination gave 2.49, required for pentane 2.49. This substance therefore corresponded to normal pentane, boiling point 37°

* Ronalds, Journ. Chem. Soc., XVIII. 54; C. M. Warren, Mem. Amer. Acad. (N. S.), IX. 156.

† Ann. Chem. Pharm., CXLIV. 10.

‡ We have since obtained 50 grams of an oil that collected at 8° to 9° with very small amounts above and below these limits. A vapor density determination by the Hofmann method gave the following result: —

0.0717 gram of the oil gave 45.5 c.c. of vapor at 16°, and under a tension of 48.1 cm. of mercury.

Required for C_4H_{10}.	Found.
2.01	2.04

For further proof as to the composition of this distillate, an examination of its halogen and other derivatives is now in progress.

(Warren). The weights collected evidently afford no information concerning the proportions in which these hydrocarbons are contained in the crude oil. Other results show that they are present in smaller quantities than in Pennsylvania oil.

At higher temperatures to 60°, the weights of the distillates were very small and irregular, which indicated the absence of definite compounds. Between 60° and 62°, 150 grams collected at the end of the fifteenth distillation, and this was still further reduced to 50 grams between 60° and 61°, with a vapor density corresponding to that of hexane; found, 2.94; required for hexane, 2.98; boiling point of isohexane, 61°.27 (Warren). After the fourteenth distillation, with the barometer at 749 mm., between 67° and 68°, 75 grams collected that distilled tolerably constant within this limit. A vapor density determination gave 3.00; required for normal hexane, 2.98; boiling point, 68°.5 (Warren).

For the separation of the less volatile hydrocarbons, the fraction —150°, obtained from the crude oil by distillation *in vacuo*, was subjected to further distillation under atmospheric pressure. 41.5 kilos of crude Findlay oil were distilled under a tension of 50 mm., and collected in the first distillation at —100°, 100°–150°, 150°–200°, 200°–250°, and 250°–350°. The decomposition was comparatively slight, and the fractions, especially the less volatile, were free from the disagreeable pungent odors characteristic of refinery distillates. Even the residue above 350° had apparently undergone very little decomposition. On account of the reduced boiling points, it was not expected that the more volatile constituents could be collected, and it was subsequently found that scarcely any distillate boiling below 30° was condensed. The weights of the first fractions were as follows: —

	—100°	100°–150°	150°–200°	200°–250°	250°–350°	Residue.
Grams	8000	8520	6480	7700	2670	9000
Percentages	18.6	19.8	15.1	18.0	6.2	20.9

The specific gravity of the individual fractions was determined with the following results: —

—100°	100°-150°	150°–200°	200°-250°	250°-350°	Residue.
0.7445	0.7941	0.8245	0.8455	0.907	0.9139

The fraction —100° contained no hydric sulphide; the higher fractions contained it in small quantities. The percentages of sulphur in the same distillates were obtained by combustion in air: —

	–100°	100°–150°	150°–200°	200°–250°	Residue.
Sulphur	0.054	0.25	0.42	0.61	0.67

In comparing the percentages of sulphur in the vacuum distillates with those under atmospheric pressure, it is evident that the main body of the sulphur compounds collects in the higher portions, leaving the fractions below 150° nearly free from sulphur.

Percentages of sulphur under atmospheric pressure: —

110°–150°	150°–220°	220°–257°	257°–300°	300°–350°	Residue.
0.10	0.38	0.41	0.37	0.37	0.54

It is also apparent that distillation *in vacuo* protects, to a certain extent, the sulphur compounds from decomposition. In ordinary distillation of the crude oil, as has been mentioned, sulphur is invariably observed in the condensing tube. Even in vacuum distillation at high temperatures decomposition cannot be wholly avoided, although the separation of sulphur has never been observed. It is probable that chemical reactions occur within the oil from the action of the various constituents upon one another, such, for example, as the action of the oxygen compounds upon the sulphur compounds. These observations are valuable evidence in favor of vacuum distillation for the sulphur petroleums.

The percentage of bromine absorbed by the fractions collected *in vacuo* was also determined: —

	–100°	100°–150°	150°–200°	200°–350°	Residue.	Crude Oil.
Bromine	0.0	4.57	6.60	7.08	24.38	10.19

It is interesting to compare the bromine absorption in the vacuum distillates with the quantities absorbed in the distillates collected under atmospheric pressure: —

	100°–150°	150°–220°	220°–257°	257°–300°	300°–330°	+330°
Bromine	0.73	1.74	4.84	5.04	12.10	19.50

Doubtless the larger absorption of bromine in the vacuum distillates at lower temperatures depends, at least in part, upon the fact that the sulphur compounds are protected from decomposition during distillation, and also upon the extent to which the constituents with higher boiling points are distilled at lower temperatures under the diminished pressure. It would be expected that the residue in the distillation under atmospheric pressure should show a higher absorptive power than that collected *in vacuo*. The behavior of the higher fractions

toward bromine and the nature of the decompositions by cracking will receive further attention.

The portions distilling below 150° were next submitted to prolonged fractional separations under atmospheric pressure with the aid of Hempel columns and Warren condensers. We were led to appreciate the exhaustive labors of our predecessors in their investigations on petroleum, and our indebtedness to them for the efficient means at present available for conducting such distillations. For the separation of complex mixtures, especially in considerable quantities, in point of efficiency the Warren condenser leaves nothing to be desired. It appears to effect a more rapid separation than the Hempel column, although the latter is of great service. The Hempel method has the advantage that it requires less attention, with no loss of time in heating a bath nor in maintaining a constant temperature in the bath. From the description of Warren's hot condenser given in the treatise on Chemistry, Vol. III. Part 1, by Roscoe and Schorlemmer, an erroneous impression must have been received concerning this apparatus. On pp. 149, 150, the following words appear: "An apparatus has been employed by Warren in the fractional distillation of tar oils and petroleums. This permits a complete control over the temperature of the vapor, accomplished by an air bath round which a spiral tube is placed, connected with the boiling flask. The temperature of this air bath is regulated by a lamp. The liquid used for heating the air bath may be either water, oil, or fusible metal, and into this the thermometer is placed. . . . In distilling petroleum the difference in temperature between the boiling liquid and the air bath was, to begin with, about 35°, or even more." The idea conveyed here is that the constant temperature is maintained by means of an air bath, although it is evident from the following description, taken from the original memoir,* that there is not the remotest allusion to an air bath: "In the new process, perfect control of the temperature of the vapors is secured by simply conducting these vapors upwards through a worm contained in a bath the temperature of which is regulated by means of a lamp, or by a safety furnace. The bath may be of oil or water or metal for very high temperatures, as the case may require, and it is furnished with a thermometer. That this bath may be equally adapted for the separation of liquids boiling below the common temperature, an empty vessel is permanently secured in the interior of the bath by means of straps of metal across the top, to

* Mem. Amer. Acad. (N. S.), IX. 125.

serve as a convenient receptacle for ice or ice water, by means of which a low temperature may be steadily maintained. This interior vessel also serves a good purpose in economizing time and fuel in heating the bath, as it diminishes the quantity of oil required to cover the worm. It is made to extend to within about three inches of the bottom of the bath, and large enough to fill a greater part of the space in the centre of the coil." It will therefore be seen that it was not Warren's intention to use this apparatus in any sense as an air bath. It is to be used solely as a liquid bath.

Since the principal object was to identify the individual constituents and to determine their approximate quantities, it was only necessary to collect our products within such close limits of temperature comparable with boiling points already accurately determined that they should yield satisfactory analytical data. In successive distillations, collecting at first within 5°, then within 2°, and finally within 1°, after the fifth distillation the fractions collected rapidly, with increasing quantities at temperatures near boiling points of well known hydrocarbons C_nH_{2n+2}, and at certain other points at which an equilibrium in boiling points seemed to be established by mixtures. It was only with much difficulty that some of these mixtures could be separated into their constituents. We had occasion to recall the remark of Warren concerning the greater amount of labor involved in determining the absence of definite compounds in such mixtures than in proving the presence of well defined hydrocarbons. The fractions containing the aromatic hydrocarbons will be considered together. The products collected for vapor density determinations were purified as completely as possible by the removal of unsaturated hydrocarbons, sulphur compounds, and the aromatic hydrocarbons. For the removal of sulphur compounds, each fraction was thoroughly agitated with alcoholic mercuric chloride. After washing with water, there remained in solution not more than 0.02 or 0.03 per cent of sulphur when the mercuric chloride gave a crystalline precipitate, which was the case in distillates below 150°, provided they were collected at first *in vacuo*. In a former paper * it was stated that alcoholic mercuric chloride removed two thirds of the sulphur. Those experiments were made with refinery distillates, which do not behave the same towards mercuric chloride as vacuum distillates. In higher fractions somewhat more sulphur is retained, and with increasing boiling points even the mercury itself in considerable quantity may be held in clear solution, either in the form of

* Amer. Chem. Journ., 1894, p. 88.

$HgCl_2R_2S$, or in some other combination. This peculiarity has occasioned us much trouble in purifying distillates above 200°. In some of these products, hydric sulphide in the cold will not precipitate the mercury; frequently it is only after prolonged action with the aid of heat that the mercury can be completely removed. These sulphur oils seem to possess the property of dissolving metals, metallic oxides, and other compounds, which has been observed in other petroleums. The action of paraffine oils on metals has been examined by Macadam,* who finds that lead, solder, and zinc are quite readily, tin and iron but slightly, affected. Some oils have a greater solvent action than others, and Macadam attributes it to the hydrocarbons. Engler † repeated the experiments of Macadam, and observed that metals were not affected when air is excluded. It was therefore inferred that acid compounds are formed in the oil by exposure to air, and also metallic oxides, which are dissolved by the acids. Engler does not attribute the solvent action to ozone. It is probable that the purification of refinery distillates from the sulphur petroleums, by agitation with an alkaline solution of plumbic oxide, depends, at least in part, upon the solvent action of certain constituents of the oil. Oxygen compounds, which are doubtless present in these oils, may assist the action, as has been observed in other oils. This subject will receive further attention when we reach the higher distillates.

After removal of the sulphur compounds, each distillate for vapor density determination was thoroughly agitated, first with concentrated nitric, then with concentrated sulphuric acid, washed, and dried. Finally, under a return condenser, it was heated for some time with metallic sodium.

From 41.5 kilos distilled *in vacuo*, at the end of the eighth distillation, the last seven under atmospheric pressure, the following weights were obtained with much smaller quantities outside these limits: —

	–55°	58°–62°	65°–68°	77°–83°
Grams	15	120	310	85

As already mentioned, on account of loss from the diminished pressure, as well as the unavoidable loss in any distillation, the weights of the lower fractions collected *in vacuo* evidently cannot be accepted as representing even approximately the quantities present in the crude oil.

* Journ. Chem. Soc., 1878, p. 355.
† Ber. der deutsch. chem. Gesellsch., 1878, p. 2186.

Between 87° and 93°, 80 grams collected after the sixth distillation, and in the portion which distilled constant at 89°–90°, bar. 754 mm., a vapor density determination gave 3.43; required for isoheptane, 3.46; boiling point, 90°.4 (Warren).

At the end of the sixth distillation, 175 grams collected at 96°–99°, and 50 grams distilled constant at 96°–97°, bar. 744 mm.; a vapor density determination of this product gave 3.42; required for heptane, 3.6; boiling point of heptane, 98°.7 (Warren). Above this point the distillates were small in amount to 109°, where other products began to appear; between this limit and 120° the single degree fractions were considerable in quantity.

At 118°–120°, 120 grams were collected, of which 50 grams distilled constant at 119°–120°, bar. 749 mm. This product gave a value in a determination of its vapor density required for octane: found, 3.98; required, 3.94. Since some doubt has been expressed concerning the existence of an octane with this boiling point, this fraction was carefully purified for analysis with alcoholic mercuric chloride, nitric acid, and sulphuric acid, and it was finally submitted to prolonged boiling with sodium. Determinations of carbon and hydrogen then gave the following results: —

I. 0.1707 gram of the oil gave 0.5282 gram CO_2, 0.1707 gram H_2O.
II. 0.2017 gram of the oil gave 0.6237 gram CO_2, 0.2737 gram H_2O.

	Calculated for C_8H_{18}.	Found. I.	Found. II.
C	84.20	84.42	84.28
H	15.79	15.19	15.08

The low percentage of hydrogen evidently indicated that the octane was still contaminated by a hydrocarbon containing less hydrogen. For further purification the oil was heated to boiling during several hours with a mixture of nitric and sulphuric acids, and boiled several times with sodium. It then gave the percentages of carbon and hydrogen rquired for octane: —

	Required for C_8H_{18}.	Found.
C	84.20	84.20
H	15.79	16.10

There seems to be no question that the fraction 118°–119° contains a hydrocarbon with the composition required for octane, and this observation is apparently confirmed by the results of others. War-

ren* separated a constituent of Pennsylvania petroleum distilling constant at 119°.5 (cor.), which gave a vapor density corresponding to that of octane. From the extraordinary care with which the determinations of Warren were made, there can be no doubt as to the existence of a hydrocarbon with this boiling point in Pennsylvania petroleum. Although hexahydroisoxylol has been recognized by Beilstein and Kurbatoff,† it is probably not the principal constituent with this boiling point of the Pennsylvania oil; it is certainly not of the Ohio oil.

From coal oil, Schorlemmer ‡ separated an octane boiling at 119°–120°, and subsequently he identified the same body in petroleum boiling at 119°. The following data are taken from his original publication: —

	Required for C_8H_{18}.	Found.
C	84.20	84.10
H	15.79	16.10
Vapor density	3.98	3.95

In the treatise on Chemistry by Roscoe and Schorlemmer, New York, 1886, it is stated that the three octanes known are normal octane, boiling point 125°.46, found in petroleum; tetramethylbutane, boiling at 108°.5; and hexamethylbutane, melting at 96°–97° and boiling at 105°–106°. This enumeration does not recognize an octane boiling at 119° in petroleum. It would seem that our fraction from the Ohio oil was prepared with sufficient care to preclude the possibility of a mixture of higher and lower constituents. We shall endeavor to obtain independent evidence as to the identity of this fraction by a study of its chemical reactions, and the preparation of its derivatives.

The following suggestion, which I have taken from one of the private papers, dated 1868, of Mr. Warren, through the kindness of Professor Storer, indicates that Warren recognized the possibility of a series containing less hydrogen: "The samples analyzed may have contained traces of more highly carbonized substances, and that it would be worth while to treat with $HOSO_2$ and $HONO_5$, and remove these." Beilstein and Kurbatoff met with the same difficulty in the fractions 95°–100° and 118°–120° in their attempts to ascertain the

* These Proceedings, XXVII. 78.

† Ber. der deutsch. chem. Gesellsch., 1880, p. 2028.

‡ Journ. Chem. Soc., XV. 419.

presence in the Pennsylvania oil of the hexahydro series. The series with less hydrogen seems to be removed only very slowly, even by vigorous treatment with a mixture of nitric and sulphuric acids.

In continuing the separations above 120°, after the eleventh distillation the oils collected in considerable quantities within the limits of one degree:—

	120°–121°	121°–122°	122°–123°	123°–124°	124°–125°	125°–126°	126°–127°	127°–128°
Grams	35	40	80	70	75	75	60	40

Notwithstanding our endeavors to separate the fraction 122°–125° into higher and lower constituents, they may still be mixtures; aromatic derivatives are here present in small quantity. If in more prolonged separations distillates still persist within the same limits, they will be submitted to careful study in their behavior toward chemical reagents.

The greater portion of the fraction 125°–130° was unfortunately lost by an accident after the eleventh distillation. Sufficient however was collected at 127°–128° for a vapor density determination; it gave, by the method of Dumas, the value required for the formula C_8H_{18}; found 3.90, required 3.94. To the liquid collected by Warren at this point was assigned the boiling point 127°.6; the vapor density found by him was 3.99, and those observations seem to be confirmed by our results with the Ohio product. The portions distilling between 115° and 130° evidently need to be carefully examined in larger quantities with particular reference to the octanes. The distillates collected between 130°–145° will be considered in connection with the aromatic compounds.

Between 144° and 148°, after many distillations, the fractions were small in quantity. At the end of the sixth distillation, 65 grams collected at 149°–151°, of which 40 grams distilled constant at 149°–150°, bar. 756 mm. After prolonged heating with concentrated nitric acid a nitro-compound was formed that remained chiefly in solution in the oil. Upon dilution of the acid an oily liquid separated in small quantities. But when the oil was shaken with sodic hydrate, it became intensely red in color, and by repeated washing with the alkaline solution the nitro-product was in part removed, and it separated again as an oil by acidifying the solution. After washing, the remaining oil was dried and heated to boiling during several hours with sodium. It was then distilled from the large quantity of solid that had separated, and the greenish yellow distillate again boiled with sodium. Still more solid separated, and after distillation the oil was

again treated with sodium until there was no further action. The boiling point was not appreciably changed by this treatment, although it was evident that some constituent had been removed capable of forming a nitro-derivative soluble in alkalies. The residual oil was shown by vapor density determinations and analysis to have the composition required for nonane. The boiling point of nonane is 150.8° (Warren).

I. 0.1799 gram of the oil gave 0.3987 gram CO_2, and 0.1749 gram H_2O.

II. 0.1751 gram of the oil gave 0.5424 gram CO_2, and 0.2488 gram H_2O.

	Calculated for C_9H_{29}.	Found. I.	Found. II.
C	84.37	84.96	84.48
H	15.63	15.16	15.88

Analysis I. was made of the oil after treatment with alcoholic mercuric chloride, but before heating with the acid mixture; analysis II. of the oil after treating with a mixture of nitric and sulphuric acids and boiling with sodium.

The determinations of vapor density of this product in the apparatus of Victor Meyer, with a bath of ethyl benzoate$_3$ gave the following results: I. 4.73; II. 4.74; required for C_9H_2O, 4.43.

This fraction therefore contains nonane, although it consists to a very considerable extent of another hydrocarbon, which seems, by the ready formation of nitro compounds and its behavior toward alkaline solvents, to be a member of the series C_nH_{2n}. All the fractions of Ohio oil that we have examined below 150° are similarly contaminated by, or rather contain in appreciable quantities, hydrocarbons which form nitro products with the characteristic qualities of the unsaturated or paraffine nitro compounds.

Thus far Ohio petroleum has proved to contain members of the series C_nH_{2n+2}, corresponding to those which have been identified in Pennsylvania oil, but in much smaller quantities. They form one fifth of crude Pennsylvania oil and less than one tenth of Ohio oil.

In identifying these constituents it has not seemed necessary to accumulate data further than would appear essential in showing the similarity of our products to those whose composition has been so carefully demonstrated in Pennsylvania petroleum. And while this portion of our labor may be of less interest than the study of the constituents with higher boiling points, it has seemed of sufficient

importance to justify the necessary expenditure of time and effort. The higher fractions have been quite thoroughly distilled entirely *in vacuo* to avoid decomposition so far as possible, and these products, as well as the residue above 350° of the first vacuum distillate, are reserved for later study.

Aromatic Hydrocarbons.

Series C_nH_{2n-6}.

So far as I am aware no attempts have hitherto been made to separate the aromatic hydrocarbons from the Ohio sulphur oil. In American petroleum Pelouze and Cahours found, as already mentioned, no appreciable quantities, but Schorlemmer recognized the presence of benzol and toluol. Beilstein and Kurbatoff were the first to discover the aromatic hydrocarbons in the oil from Baku, and hexahydroisoxylol in Pennsylvania petroleum.

Benzol.

After the sixth distillation of the products from the original quantity of crude oil, twenty-five grams collected at 77°–79°, 35 grams at 79°–81°, and 20 grams at 81°–83°. In each of these fractions the quantity of benzol was determined by heating carefully for some time a weighed quantity of the fraction with a mixture of nitric and sulphuric acids, distilling off the portion not affected by the acid mixture, and weighing it and the residual nitrobenzol. The fraction 77°–79° gave by this method 3 per cent of benzol; the fraction 79°–81°, 15 per cent; and the fraction 81°–83°, 5.8 per cent. The fraction 75°–76° and 85°–86°, when treated in the same manner, left scarcely any residual product after distillation, and after reduction with tin and hydrochloric acid not a trace of color was visible in applying the exceedingly delicate furfurol reaction for aniline. Calculating from these numbers, the quantity of benzol in the 41.5 kilos of crude oil taken, it amounts to 7.16 grams or 0.017 per cent, which represents approximately the quantity of benzol in the crude oil.

Toluol.

The fractions collected between 107° and 113°, after the sixth distillation under a Hempel column, were examined for toluol by treating a weighed quantity of the oil with nitric and sulphuric acids, keeping the solution cold. After some time crystals of dinitrotoluol separated, and when the hydrocarbons not affected by the acid were

removed by distillation, there remained a heavy oil which consisted of the liquid orthonitrotoluol and crystalline dinitrotoluol. The latter soon solidified, and after crystallization from alcohol it was identified by its melting point, 71°. The loss in weight by the removal of toluol in the fraction 107°–109° amounted to 1.14 per cent, in the fraction 109°–111° to 13.07 per cent, and in the fraction 111°–113° to 2.8 per cent. The total weight of the first fraction was 50 grams, of the second 80 grams, and of the third 65 grams. These fractions, therefore, contained altogether 12.85 grams, which corresponds to 0.03 per cent of toluol in the 41.5 kilos of crude oil taken. As in the case of benzol, evidently the percentage of toluol is expressed only approximately by these results. After longer distillation the fraction 114°–115° was treated in a similar manner, but after treatment with nitric and sulphuric acids, and with tin and hydrochloric acid, the product which remained in considerable quantity after distillation did not dissolve in hydrochloric acid, and it gave no trace of color when heated with ferric chloride or with mercuric chloride. The insolubility in acids excludes in this fraction any appreciable quantity of hexahydroisoxylol which is contained in the higher portions. The oily product of the nitration must therefore be derived from another series, perhaps from an unsaturated hydrocarbon C_nH_{2n}; it will receive further attention.

Xylols.

In the first allusion to the presence of the aromatic hydrocarbons in petroleum, by De La Rue and Müller,* who found in the Rangoon oil benzol, toluol, metaxylol, and cumol, there is no evidence that the isomeric forms of xylol were discovered in that petroleum. Except paraxylol, which Pawlewski found in Galician petroleum and Engler in Pennsylvania petroleum, and metaxylol, which is generally found, it does not appear that the isomeric xylols have elsewhere been recognized in petroleum.

Between 136° and 142° in our distillates, at intervals of one degree we collected 205 grams, of which the greater portion distilled at 137°–138°, 139°–140°, and 141°–143°. After prolonged distillation these fractions collected in increased quantities at these points; they were readily acted upon by nitric acid, forming nitro compounds or oxidation products, according to the form of the reaction.

To prove the presence of paraxylol in fraction 137°–138°, a portion was treated with a mixture of nitric and sulphuric acids, at first in the

* Proc. Roy. Soc., 1856, p. 221.

cold, then with the aid of a gentle heat. Upon distillation of the hydrocarbon not affected, there remained a brown oil that deposited a crystalline product on standing. After crystallization from alcohol, this substance appeared in the form of glistening white needles which melted at 139°–140°. It was therefore trinitroparaxylol, melting point 139°–140°.* By treating carefully another portion of the same fraction in the cold with fuming nitric acid, long yellow needles sparingly soluble in alcohol were obtained, melting at 145°, corresponding to dinitroparaxylol, melting point 147°–148°.† For further confirmation, another portion of the fraction 137°–138° was submitted to oxidation with chromic acid, and the solution extracted with a considerable quantity of ether. Evaporation of the ether left a solid residue in the form of minute prisms insoluble in water, but readily soluble in sodic hydrate. This substance sublimed without melting, and in general its properties corresponded to those of terephthalic acid. After heating for thirty hours a quantity of the same fraction with dilute nitric acid and distilling off the hydrocarbon not affected, there remained an oily product which contained no toluic acid. In repeating this experiment with longer heating, on cooling an oily layer separated above the acid, which was neutralized with sodic hydrate, evaporated to dryness, the salt decomposed with hydrochloric acid, and the solution extracted with ether. Upon evaporation a crystalline solid was left, but not in sufficient quantity for further examination; it was probably paratoluic acid.

In the fraction 139°–140° metaxylol was recognized by the formation of the trinitro-compound. A portion of the oil was heated with a mixture of nitric and sulphuric acids during forty-eight hours, the oil together with the crystals which formed was separated from the acid solution, the oil distilled, and the solid remaining with the first crystals was purified by crystallization from hot alcohol; on cooling, long slender colorless needles separated, melting at 175°–176°. This nitro compound was therefore trinitrometaxylol, melting point 176°. Several different melting points have been assigned to trinitroxylol. Luhman ‡ gave 177°, and Tilden § 182°. To explain the latter result Tilden asserted that the lower value of Luhman was due to contamination of the trinitroxylol by the isomeric nitro compounds derived

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* Nölting and Geissman, Ber. der deutsch. chem. Gesellsch., XIX. 145.

† Lellmann, Ann. Chem. Pharm., CCXXVIII. 250.

‡ Ann. Chem. Pharm., CXLIV. 274.

§ Journ. Chem. Soc., XLV. 416.

from coal tar, the source of the metaxylol from which the trinitro compound was prepared. But in the preparation of this trinitro derivative from octonaphtene, Markownikoff and Spadi * gave 179°–180° as its melting point.

An approximate quantitative determination of metaxylol was made in the fraction 139°–140° by heating a portion during one hour with dilute nitric acid, which should oxidize the para- and ortho-xylols to the corresponding toluic acids, and the remaining oil was washed with water, dried, and distilled with steam. The decrease in volume was noted, and it corresponded to 6.3 per cent of the quantity taken. The distillate was next shaken with concentrated sulphuric acid, which dissolves metaxylol, and the decrease in volume corresponded to 16.6 per cent of metaxylol. In determining the quantity of paraxylol, a weighed amount of the fraction 137°–138° was shaken thirty minutes with concentrated sulphuric acid to dissolve the ortho- and meta-xylols, with a loss in volume equivalent to 4 per cent of the quantity taken. The residual oil was then agitated with fuming sulphuric acid, and the diminished volume represented 12.2 per cent of paraxylol.

In attempting to ascertain the presence of orthoxylol, dependence was placed upon the observation of Jacobsen, that a single drop of orthoxylol may be distinguished in a mixture of the three isomers by treating them in the cold with a mixture of nitric and sulphuric acids. The fraction 142°–143° gave immediately an oily layer in considerable quantity between the acid and the lighter oil, which should be the liquid orthonitroxylol. The fraction 139°–140° gave no trace of an oily layer even after long standing. By further treatment with the acid mixture with the aid of heat, the oily mononitro product from distillate 142°–143° was converted into a crystalline dinitro compound melting at 91°, the melting point of dinitrometaxylol. By long continued action of the acid mixture, hot, a trinitroxylol was formed, nearly insoluble in alcohol, and melting at 178°, which might be a derivative either of ortho- or meta-xylol. Another portion of the distillate 142°–143° was heated with dilute nitric acid, which should form orthotoluic acid without affecting metaxylol. Upon extracting the acid solution with ether, an oily residue remained after evaporation of the ether with the characteristic odor of toluic acid, but no crystals separated even after long standing. An attempt was made to separate the less soluble sodic orthoxylol sulphonate, but upon evaporation of

* Ber. der deutsch. chem. Gesellsch., 1887, p. 1850.

the solution no crystalline product appeared until the solution was so far concentrated that the sodic metaxylol sulphonate was deposited. Orthoxylol cannot therefore be present in any appreciable quantity.

Determinations of the constituents capable of forming nitro products were also made in the fractions containing the xylols by treatment with a mixture of nitric and suphuric acids according to the method employed for benzol and toluol. The quantity of xylol corresponding to the nitro product represented by the portion not affected by nitric acid in the fraction 137°–138° was 54.3 per cent of the weight of oil taken; in the fraction 139°–140°, 72.1 per cent; and in fraction 141°–143°, 31.5 per cent. Calculating the percentages of xylols from the results of the first determination in the 41.5 kilos of crude oil first distilled, the quantity of metaxylol is 0.016 per cent, and of paraxylol, 0.013 per cent. Evidently the xylols were not wholly collected in their respective fractions, although the quantity outside of the limits, 137°–143° was doubtless small. Probably at least one third should be added to these results. But if the percentages were increased to the results obtained by the action of concentrated nitric acid, the quantities of the xylols in the crude oil would still be small. In the fractions 132°–136° we observed the presence of aromatic hydrocarbons, although in too small amounts for identification; nitro products were formed by the action of nitric acid. Attempts were made to ascertain the presence of ethylbenzol and hexahydromesitylene, but without success, on account of the limited quantity of the distillates. After treatment of the fraction 135°–136° with concentrated nitric acid to convert the hydrocarbons C_nH_{2n-6} into nitro products, and distilling off the hydrocarbons not affected by the acid, the distillate was heated for some time with a mixture of nitric and sulphuric acids. According to Baever,* fuming nitric acid readily converts hexahydromesitylene into trinitromesitylene; but Konowaloff † found that a mixture of nitric and sulphuric acids, or fuming nitric acid, forms the trinitro compound only very slowly. After prolonged heating we obtained a crystalline nitro compound, but in such small quantity that it was impossible further to identify it. A much larger supply of these distillates will be necessary to determine the presence of these bodies.

* Ann. Chem. Pharm., CLV. 275.

† Ber. der deutsch. chem. Gesellsch., 1887, p. 1850.

Series C_nH_{2n}.

Hexahydro compounds (Beilstein and Kurbatoff); naphtenes (Markownikoff and Ogloblin).

The lower members of this series include: —

Hexahydrobenzol, C_6H_{12},	boiling point, 69°.
Hexahydrotoluol, C_7H_{14},	boiling point, 97°.
Hexahydrocumol, C_9H_{18},	boiling point, 147°–150°.
Hexahydrocymol, $C_{10}H_{20}$,	boiling point, 171°–173°.
Hexahydroisoxylol, C_8H_{16},	boiling point, 118°.
Hexahydromesitylene, C_9H_{18},	boiling point, 135°–138°.

In examining Ohio petroleum for the lower hydrocarbons of this series, the fraction 69°–70°, after the fourteenth distillation, was shaken with concentrated nitric acid, then with concentrated sulphuric acid, and finally heated with metallic sodium. Determinations of carbon and hydrogen in the purified oil gave results corresponding to the composition of hexane: —

I. 0.1618 gram of the oil gave 0.4934 gram CO_2, and 0.2299 gram H_2O.

II. 0.1891 gram of the oil gave 0.5790 gram CO_2, and 0.2663 gram H_2O.

	Required for		Found.	
	C_6H_{14}.	C_6H_{12}.	I.	II.
C	83.72	85.71	83.18	83.51
H	16.28	14.28	15.79	15.65

Hexahydrobenzol is therefore not present in appreciable quantities in Ohio petroleum.*

The fraction 96°–97°, bar. 750 mm., after the fourteenth distillation, was purified as before, and the composition determined by analysis: —

* Recently Markownikoff (Ber. der deutsch. chem. Gesellsch., 1895, p. 577) has ascertained that hexanaphten (hexahydrobenzol) which he formerly reported as a constituent of Caucasus naphtha, boiling at 69°–71°, is not a single body. Since the discovery by Baeyer of hexamethylen, boiling point 79°, Markownikoff has discovered that Caucasus naphtha contains rather this same hexamethylen which he has identified by the formation of its nitro products. It will, therefore, be necessary to examine more carefully the corresponding distillates from the oils we have under examination for this body.

I. 0.2083 gram of the oil gave 0.6423 gram CO_2, and 0.2849 gram H_2O.

II. 0.2010 gram of the oil gave 0.6200 gram CO_2, and 0.2744 gram H_2O.

	Required for		Found.	
	C_7H_{16}.	C_7H_{14}.	I.	II.
C	84.00	85.71	84.09	84.72
H	16.00	14.28	15.27	15.17

This oil was evidently heptane contaminated, as shown by the low percentage of hydrogen, by a hydrocarbon containing less hydrogen. To remove any doubt as to the presence of heptane, the oil was heated during fifteen hours with a mixture of nitric and sulphuric acids, the oil separated from the acid, washed, dried, and boiled for some time with sodium. It was then distilled from the large amount of colored residue, again boiled with sodium, and distilled. The last distillation left very little residue, and the distillate was nearly odorless. The residue from the treatment with sodium crystallized well from alcohol. Upon diluting the acid a heavy nitro product separated in considerable quantities. A combustion of the purified oil gave the following percentages of carbon and hydrogen: —

0.1410 gram of the oil gave 0.4224 gram of CO_2, and 0.2065 gram H_2O.

	Required for C_7H_{16}.	Found.
C	84.00	83.75
H	16.00	16.28

In a distillate 95°–100° from American ligroine, Beilstein and Kurbatoff* found 84.8 per cent of carbon and 15.4 per cent of hydrogen. After prolonged heating with nitric acid, the oil distilled at 98°.5 – 99°.5, and gave on analysis 84.2 per cent of carbon and 15.9 per cent of hydrogen, from which it was inferred that hydrocarbons poorer in hydrogen were contained in the crude ligroine. A nitro derivative was separated from this fraction with the composition of nitropropane, $C_7H_{15}NO_2$. The fraction from Ohio petroleum gave no nitro compound when treated with nitric acid, and the acid was diluted.

Scarcely any residue remained when the oil was distilled after the treatment with acid. With a mixture of nitric and sulphuric acids, as shown above, much nitro compound separated upon dilution, which was

* Ber. der deutsch. chem. Gesellsch., 1880, p. 2028.

soluble in potassic hydrate like the nitro derivatives of the series C_nH_{2n+2}, and by boiling with sodium the solid residue was large.

In distillates 85°–105° from Bibi-Eibat and from Balakhani, after thirty fractional separations, Milkowsky * collected a body that distilled constant at 100°–101°, and by the formation of its halogen derivatives proved it to be heptanaphtene. The oil boiling at 101°–103°, which Beilstein and Kurbatoff separated from Baku oil, was doubtless the same product, but Beilstein and Kurbatoff considered it to be composed for the most part of hexahydrotoluol, boiling point 97°.

Hexahydroisoxylol was found by Beilstein and Kurbatoff in Caucasus petroleum,† and in American ligroine; ‡ since the American source was not mentioned, it is to be inferred that the ligroine was prepared from Pennsylvania oil. In testing the fractions 118°–119°, fourteenth distillation in a Hempel column, for hexaisoxylol, a portion of the oil was heated forty hours with a mixture of nitric and sulphuric acids. The nitro product separated from the oil when cold in long, flat plates, nearly insoluble in cold, more readily in hot alcohol. When purified by crystallization, this substance melted at 177°, and was, therefore, trinitroisoxylol. A similar crystalline nitro product with the same melting point was found in the fraction 123°–124°. Since the prolonged distillation precluded the possibility that this fraction contained metaxylol, there can be no doubt that the trinitroxylol obtained from fraction 118°–119° indicated the presence of hexahydroisoxylol, although it evidently formed only a small proportion of this product. After a portion of the same distillate was agitated thoroughly with a mixture of nitric and sulphuric acids, and distilled over sodium, analysis gave the percentages of carbon and hydrogen required for octane, as has been shown (page 30): —

	Required for		Found.		
	C_8H_{18}.	C_8H_{16}.	I.	II.	III.
C	84.20	85.71	84.42	84.28	84.20
H	15.79	14.28	15.19	15.08	16.10

As already explained, Analysis III. was made after prolonged treatment with the mixture of acids by which the hexahydro compound is removed very slowly, and the final results show that the fraction is composed chiefly of the more highly hydrogenized hydrocarbon, although it contains a considerable quantity of the other constituent, as shown by the abundant formation of nitro product.

* Ber. der deutsch. chem. Gesellsch., 1885, c. 187.

† Ibid., 1880, p. 1818.

‡ Ibid., p. 2088.

In the intermediary product from the separation of octonaphtene and nononaphtene, by prolonged boiling with sodium and treatment with fuming sulphuric acid, Putochin * obtained a hydrocarbon distilling at 122°–124°, principally at 122°.5, which corresponded in its composition to the formula C_8H_{18}. It gave a chloride different from the corresponding derivative of octonaphtene, and it was therefore accepted as isooctonaphtene. By treatment of the chloride with alcoholic potassic hydrate, isooctonaphtylene was formed with a higher boiling point than naphtylene from octonaphtene.

The principal features of the Ohio sulphur petroleum which have appeared in the course of this examination are the following.

1. The crude oil is heavier than the Pennsylvania, and lighter than the Russian oil. In the quantities of the higher distillates, and in its general properties it resembles more nearly the latter.

2. It differs from other petroleums in the large amounts of sulphur compounds which exert an influence on the general properties of the oil.

3. It resembles the Pennsylvania oil in containing below 150° members of the series C_nH_{2n+2}, although in much smaller quantities. The presence in the Ohio oil of the two isomeric series C_nH_{2n+2} confirm the observations of Warren on the Pennsylvania petroleum.

4. The aromatic hydrocarbons are here present in minute quantities, apparently much smaller than in other petroleums. Benzol, toluol, meta- and para-xylol have been identified. The hexahydro series C_nH_{2n} is represented by hexahydroisoxylol, and very probably by higher members, although this has yet to be determined. Hexahydrobenzol and hexahydrotoluol are not contained in this petroleum.

5. By the formation of characteristic nitro products, and the results of bromine absorption, the presence in the crude oil of unsaturated hydrocarbons C_nH_{2n} seems to be indicated.

Portions of Ohio petroleum have been thoroughly fractioned, and are now under examination to establish the identity of the octanes, to ascertain whether isooctonaphtene and hexahydromesitylene are present, and to ascertain whether this petroleum contains α-nonane, boiling point 135°–137°, and β-nonane, boiling point 129°.5 – 131°.5, which Lemoine † asserts is contained in Pennsylvania petroleum. Examination of distillates collected above 150° is now in progress.

* Ber. der deutsch. chem. Gesellsch., 1885, p. 186.

† Bull. Soc. Chim., 1884, XLI. 164.

Canadian Petroleum.

Closely connected with the chemistry of Canadian petroleum are certain features relating to its occurrence, and the associated geological formations, which have not been fully investigated. The deposits of petroleum in Canada have been longer known than those in the Lima and Findlay fields in Ohio. As early as 1857 the existence of oil in considerable quantity in the township of Enniskillen was ascertained, and in 1862, the first flowing well was started. It was estimated by Dr. Winchell * that during the summer of 1862 not less than 5,000,000 barrels of oil flowed off on the waters of Black Creek. The flow of these early wells was very large. At a depth of 188 feet as much as 6,000 barrels of oil daily escaped from a single well, and at 237 feet 7,500 barrels daily, nearly equal to the flow of the great wells at Baku.

It is now known that these deposits of oil were mainly in the form of "pockets," and they formed no part of the main fields which are still productive. This oil territory is situated on two parallel anticlinals, about ten miles apart, with the corresponding synclinal between, from which no oil is obtained. In various reports of these oil fields, the larger area of oil-bearing strata at Petrolia is given as twenty-seven square miles, but the really productive field is actually contained within an area of less than eight square miles. The productive field at Oil Springs is included within an area of less than two square miles. The oil deposits are here found in the Corniferous limestone underlying the Hamilton group of shales and limestones. Unlike the Trenton oil rock in Ohio, the oil-bearing limestone is quite near the surface; the usual depths of wells at present in the Petrolia field is 465 feet.

I am indebted to the experience and extended observations of Messrs. M. G. Woodward of Petrolia and F. J. Carman for valuable information concerning the geological features and technology of the Canadian oil, of which a more detailed account will elsewhere be given.†

Under the general title of American petroleum, with occasional reference to Pennsylvania and to Canada as the particular sources, several partial examinations of crude Canadian oil were early made by French and English chemists. The first examination of Canadian

* Geological Report of Canada, 1888–89.

† A paper soon to be presented at the Franklin Institute.

oil was undertaken by Pelouze and Cahours * for the purpose of separating and identifying the hydrocarbons therein contained. Their attention was confined to the series C_nH_{2n+2}, and published accounts of their work contain no allusion to any other constituents than this series of hydrocarbons. They failed to observe the presence of aromatic hydrocarbons, although, as already mentioned, Schorlemmer discovered the presence of the benzol hydrocarbons in "real Canadian rock oil, a thick black liquid of a very unpleasant odor."

My attention was first attracted to Canadian petroleum in 1890, when I procured some of the crude oil and also a quantity of the "sludge" from the refining of burning oil, for the purpose of examining the sulphur compounds. The peculiar features of the distillates in a preliminary examination † invited further attention, and I determined to undertake, with the aid of the refiners, as complete an examination as was possible with the appliances at my command. It may seem somewhat surprising that such an examination of the sulphur petroleums in general has not previously been undertaken; but it should be borne in mind that it requires the facilities of a well equipped organic and technological laboratory for the manipulation of considerable quantities of material, and a corps of efficient chemists with aid from the refinery of crude oils, partially refined products, and residues. Even with all necessary accessories, aside from the tedious routine labor, there are certain features of decomposition and slow separation of constituents that render this work extremely difficult. In view of possible changes in the composition of petroleum, in the course of time, as wells become exhausted or the oil is taken from different depths, or indeed with the possibility of future exhaustion of oil fields which at present appear to be in the zenith of their production, it would seem that a comprehensive study of these oils should not be too long delayed.

From the peculiar nature of petroleum and its numerous constituents, all of which, so far as they have been examined aside from the lighter hydrocarbons of the series C_nH_{2n+2}, or the series C_nH_{2n}, are present in small quantities, any attempt toward a separation of these constituents involves the manipulation of large volumes of the oils in such a manner as to prevent so far as possible decompositions, which cannot be entirely avoided even with the greatest care. On this account satisfactory results can be hoped for only in products that have

* Bull. Soc. Chim., 1863, p. 228.

† Amer. Chem. Journ., 1894, p. 89.

been obtained, at least in part, in experiments with several hundred barrels of oil, which must be performed with the aid of the appliances in a refinery. On the other hand, an examination of the unstable sulphur oils for certain constituents can be carried on satisfactorily only on a smaller scale, with laboratory appliances.

The products which I obtained through the aid of Messrs. Samuel Rogers & Co., of Toronto, and Mr. J. H. Fairbanks, of Petrolia, for the study of Canadian petroleum, included a barrel of crude oil, considerable quantities of the first distillate, naphtha distillate, and burning oil distillate, none of which had been further refined, besides 200 litres of thoroughly washed sulphur oil from "sludge." The crude oil was thick and nearly black in color; it contained hydric sulphide in small quantity, and some water, which was removed only after long standing in intimate contact with fused calcic chloride, and even then a small quantity appeared in the first distillate. A determination of its specific gravity at 20° gave 0.8621. In a former determination in another quantity of the crude oil we reported 0.8600.* Determinations in other specimens gave the following results: —

Oil Springs		0.8442
"		0.8427
"	(gas oil)	0.8389
Petrolia		0.8553

These numbers are not essentially different from those reported in other examinations of these oils. H. P. Brummel † gave as the specific gravity of the Canadian oils 0.804 and 0.808, values which must be accepted as only approximate, rather than as results of accurate determinations. Markownikoff and Ogloblin ‡ referred to results of Sainte Claire Deville, which gave 0.844 as the specific gravity of Canadian oil, and 0.887 for Ohio oil. Reference to the original publication of Deville § shows that he obtained 0.870 as the specific gravity of Petrolia oil, and 0.844 for oil from "Canada West" (Oil Springs?). The numbers assigned by Redwood ‖ to the oils at Petrolia were 0.859–0.877, and to the oils from Oil Springs 0.844–0.854. As Engler observed in the Alsace oils, it is possible that the specific gravity diminishes with the depth of the well.

* Amer. Chem. Journ., 1894, p. 90.
† Canadian Geological Report, 1888–89.
‡ Ann. Chim. Phys., [6.], II. 372.
§ Comptes Rendus, LXVIII. 485.
‖ Journ. Soc. Chem. Ind., 1887, p. 405.

Determinations of sulphur in the crude oil gave the following percentages: —

	I.	II.	III.	Oil Springs.
Sulphur	0.98	0.99	1.06	0.60

Canadian petroleum contains somewhat less carbon and hydrogen than Ohio oils: —

I. 0.1908 gram of Petrolia oil gave 0.5874 gram of CO_2 and 0.2295 gram H_2O.

II. 0.1914 gram of Oil Springs oil gave 0.5868 gram CO_2 and 0.2305 gram H_2O.

	I.	II.
C	83.94	83.62
H	13.37	13.39

In the Canadian Geological Report above mentioned Brummel gave 85 per cent for carbon and 15 per cent for hydrogen. These percenttages are evidently only approximate. They do not agree with results earlier obtained by Pelouze and Cahours, who reported a considerable percentage of oxygen.*

C.	H.	O.
84.2	13.4	3.0

The variation in composition in the Canadian, Ohio, Pennsylvania, and Russian petroleums is shown in the following table: —

	Canadian.	Ohio.	Pennsylvania.	Russian.
C	83.94	84.57	84.19	86.89
H	13.37	13.62	13.70	13.18

After accounting for one per cent of sulphur in the Canadian oil and 0.70 per cent in the Ohio oil, the remaining percentage may reasonably be assigned to oxygen, yet in the Russian oils the composition is fully accounted for by the carbon and hydrogen, although the presence of oxygen compounds in considerable quantity has been demonstrated in several independent investigations.

Having an opportunity to collect fragments of the oil rock at Petrolia soon after it had been removed in drilling a well, I have ascertained its composition. Like most wells in this territory, the oil-bearing stratum was reached at a depth of 465 feet. The driller distinguishes two varieties of rock, one stratified and offering less resistance

* *Loc. cit.*

to the drill than the other, which is finer grained and for the most part loose and granular like sand. For convenience these specimens may be designated as I. and II. consecutively, and their composition is shown by the following results of analysis, to which is appended for comparison the composition of the Trenton limestone at Findlay, III., at a depth of 1,096 feet, and of the same oil rock at Lima, IV., at a depth of 1,247 feet.*

	I.	II.	III.	IV.
Calcic carbonate	49.80	49.75	53.50	52.66
Magnesic carbonate	44.35	45.44	43.05	37.53
Silicious residue	0.52	0.80	1.70	4.15
Alumina and iron	0.46	1.00	1.25	

It therefore appears that the dolomitic condition is not wanting in the oil-bearing Corniferous limestone; in fact, magnesic carbonate seems to be somewhat in excess of the quantity present in the Ohio Trenton limestone. The specimens were impregnated with oil and were thoroughly washed with gasoline to remove so far as possible the carbonaceous portion.

In a distillation of Petrolia oil under atmospheric pressure, the first distillate appeared at 115°, and the following weights in grams were obtained from 800 grams: —

	115°-150°	150°-200°	200°-250°	250°-300°	300°-350°	Residue.	Loss.
Weights	22	62.5	72	43	27	561	12
Per cent	2.75	7.8	9.5	5.1	3.1	70.1	1.75
Sp. Gr.	0.767	0.8026	0.8228	0.8345	0.9037		

In the proportions that distil at different temperatures and in the specific gravity of the distillates, the Oil Springs resembles more nearly the Findlay oil: —

	— 100°	100°-150°	150°-200°	200°-250°	250°-300°	300°-350°	Residue.	Loss.
Weights	8	41	90	62	88	47	357	7
Per cent	1.14	5.86	12.85	8.86	12.6	6.71	51.0	0.98
Sp. Gr.		0.7335	0.7675	0.7984	0.8222	0.8386	0.9032	

A comparison of the distillates at increasing temperatures from oils of different localities has been included in considering the properties of the Ohio oils. A clearer idea of the peculiar character of Canadian oil may be gained by comparing the distillates from it with

* Orton, Geological Survey of Ohio, 1890, p. 13.

those from oils of other fields. It is evident that the high specific gravity of the Canadian and Ohio crude oils depends upon constituents that do not distil below 350°. In this respect these oils differ essentially from the Russian oil, in which all the distillates show a high specific gravity. The distillates below 150° from Canadian oil are somewhat lighter than the corresponding products from Ohio crude oil. In considering later the properties of the vacuum distillates it will be seen that these proportions are very materially changed by distillation *in vacuo*.

	Apscheron.		Pennsylvania.	
	Per cent.	Specific Gravity.	Per cent.	Specific Gravity.
120°–150°	0.5		19.70	
150°–200°	10.9	0.786	8.85	0.757
200°–250°	12.8	0.824	15.23	0.788
250°–320°	24.7	0.861	20.70	0.809
	48.9		64.48	
Residue	51.1		35.52	

Canada.

	Petrolia.		Oil Springs.	
	Per cent.	Specific Gravity.	Per cent.	Specific Gravity.
— 100°			1.14	
100°–150°	2.75	0.7670	5.86	0.7335
150°–200°	7.80	0.8026	12.85	0.7675
200°–250°	9.50	0.8228	8.86	0.7984
250°–300°	5.10	0.8345	12.60	0.8222
300°–350°	3.10	0.9037	6.71	0.8386
	28.25		48.02	
Residue	70.10		51.00	

Ohio.

	Per cent.	Specific Gravity.
110°–150°	9.75	0.7282
150°–220°	16.63	0.7669
220°–257°	10.75	0.7940
257°–300°	9.75	0.8138
300°–350°	8.63	0.8242
	55.51	
Residue	43.00	

In the percentages of the lower fractions it will be seen that the Canadian oil resembles more nearly that from the Caucasus, but the

residue above 350° is much larger than in the oils from other fields. As will appear later, this difference is much less in distillations conducted *in vacuo.*

The percentage of sulphur was determined in each distillate by a combustion in air: —

	115°–150°	150°–200°	200°–250°	250°–300°	300°–350	Residue.
Sulphur	0.28	0.42	0.50	0.51	0.86	0.70

Determinations of the quantity of bromine absorbed indicated a greater capacity for absorption in the higher fractions, but less in the residue than in corresponding fractions from the Ohio oil: —

Canada.		Ohio.	
Fraction.	Per cent of Bromine.	Fraction.	Per cent of Bromine.
115°–150°	0.67	110°–150°	0.73
150°–200°	1.12	150°–220°	1.74
200°–250°	3.49	220°–257°	4.84
250°–300°	8.39	257°–300°	5.04
300°–350°	14.4	300°–330°	12.10
+ 350°	17.8	+ 330°	19.50

The Oil Springs oil differs essentially in many respects from Petrolia oil, especially in its lower specific gravity, lower percentage of sulphur, and in the proportions in which it distils at different temperatures. In certain peculiarities it approaches Ohio oil. The lower fractions show a higher bromine absorption than either the Petrolia or the Ohio oil: —

	Per cent of Bromine absorbed.
—100°	0.0
100°–150°	2.31
150°–200°	4.09
200°–250°	8.98
250°–300°	8.41
300°–350°	12.00
+ 350°	33.78

The percentage of bromine absorbed by the crude oils was also determined: —

Petrolia.	Oil Springs.	Ohio.
15.11	17.69	10.19

Hydric sulphide escaped in small quantities during the distillation, but below 200° the decomposition was slight, and the distillates were colorless. Above this point the products were somewhat colored, with the disagreeable odor of decomposition. It is probable that cracking begins near this temperature, affecting the unsaturated hydrocarbons if they are present, and perhaps other series as well as the sulphur compounds. Certain constituents of the Canada oil seemed to be more unstable than those of Ohio petroleum. The tendency toward polymerization of unsaturated hydrocarbons separated from distillates corresponding to burning oil has been observed by me.* An oil that had been distilled many times *in vacuo* and allowed to stand two years, when again heated suddenly polymerised into a higher product that could not be distilled at any temperature on account of complete decomposition. The conversion of Canadian petroleum into asphalt, upon long standing exposed to the weather, is well known. Large masses of this material may be seen in a pitchy form in the vicinity of Oil Springs.

Determinations of carbon and hydrogen were made in the coke from Petrolia oil, in one sample from the crude oil, and in another from a tar distillate with the following results: —

	Crude Oil.	Tar Distillate.
C	94.04	94.34
H	4.19	4.34

A specimen of "surface" oil was collected at Oil Springs for examination. It was very thick, with the consistency of ordinary molasses. A determination of its specific gravity at 20° gave 0.9059. It contained 0.05 per cent of nitrogen, and 0.95 per cent of sulphur. The weight of bromine absorbed was equivalent to 25.46 per cent. This oil is evidently an intermediary product in the formation of the deposits of pitch resembling asphalt, which have long been known at Oil Springs. The pitch is evidently formed by evaporation from the oil of the more volatile constituents, and its formation is doubtless due, in part at least, to polymerization of lower constituents of less stability. A combustion of this pitch gave 64.86 per cent of carbon and 8.13 per cent of hydrogen. In a determination of nitrogen 0.40 per cent was obtained, and the percentage of sulphur was found to be 0.65. The pitch contained 10.13 per cent of ash, and a qualitative examination showed that it was composed chiefly of calcic oxide, with smaller

* Amer. Chem. Journ., 1894, p. 92.

amounts of aluminic and ferric oxides, besides a trace of magnesic oxide. A determination of its bromine absorption gave 37.79 per cent.

Nitrogen was determined in each variety of coke, and in several samples of crude oil by the Kjeldahl method : —

Coke from crude oil	0.38
Coke from tar distillate	0.31
Petrolia crude	0.16
Oil Springs	0.18
Oil Springs gas oil	0.21

Sulphur was determined in the two varieties of coke, and in a specimen of crude paraffine wax :—

Coke from crude oil	0.76
Coke from tar distillate	0.76
Crude paraffine wax	0.97

When it is remembered that this coke in the process of carbonization had been exposed to a temperature closely approaching a red heat, it is not easy to understand how it could retain so large a proportion of nitrogen and sulphur. If the ash was sufficient in quantity, the presence of metallic cyanides and sulphides might be assumed. But 0.07 per cent of ash is not sufficient to account for such a high percentage of sulphur. Moreover, careful tests failed to show the presence of either sulphides or cyanides. In determinations of sulphur by combustion in air, we have frequently found that the carbon must be completely burned, otherwise the percentage of sulphur is too low.

With the purpose of ascertaining the mineral constituents of Canadian petroleum I procured a specimen of coke from the distillation of the crude oil, and another from the coking of a tar distillate. Since finely divided mineral matter is frequently held in suspension in the crude oil long after it is taken from the well, it might be inferred that the ash from the crude oil should consist in part of suspended material. The specimen selected was a part of a large fragment, one side of which had evidently been carbonized in contact with the bottom of the still. The portion for analysis was taken from the opposite side, which had evidently been carbonized several inches above the bottom. The residue from combustion in oxygen corresponded in the crude oil coke to 0.17 per cent, and in the coke from the tar distillate to 0.07 per cent. These quantities of ash correspond to 0.012 per cent in the crude oil. An examination of the ash showed that it was composed of

the oxides of magnesium, calcium, iron, and aluminum. It consisted chiefly of the oxides of calcium and magnesium, doubtless derived from the dolomitic reservoir.

A quantity of brine was collected for examination at Petrolia from a well recently drilled. Analysis showed that it contained calcic sulphate, and calcic, magnesic, and sodic chlorides, in the following proportions in 1,000 parts: —

$NaCl$	10.71
$MgCl_2$	2.90
$CaCl_2$	1.20
$CaSO_4$	3.20
Iron and alumina	traces.
	18.00

The specific gravity of this brine at 20° was 1.0165.

The composition of this brine is quite different from that given in the early history of this oil territory by Dr. T. Sterry Hunt. We made no examination for potassic chloride. 1,000 parts of the brine gave in Hunt's analysis: —

$NaCl$	4.800
KCl	0.792
$CaCl_2$	12.420
$MgCl_2$	3.650
	21.662

It is practically impossible, at least in glass, to distil the Canadian oil on a small scale unless it is free from water, and the water can be removed only by long standing with large quantities of calcic chloride.

After the first distillation there is less difficulty in removing water except in the least volatile distillates. The necessity of vacuum distillation to avoid decomposition was even more evident in Canadian than in Ohio oil. In quantities of 12 litres each, 64.5 kilos were distilled in a porcelain still under a tension of 50 millimeters, and the following quantities of the distillates were collected at different temperatures: —

	— 100°	100°-150°	150°-200°	200°-250°	250°-300°	300°-350°	Residue
Grams	3870	7288	7159	8578	7869	6698	22059
Per cent	6.00	11.3	11.1	13.3	12.2	10.4	34.2
Per cent in Ohio oil	18.6	19.8	15.1	18.0	250°-350° 6.2		20.9
Sp. Gr.	0.7549	0.7852	0.8161	0.8387	0.8647	0.8759	0.9189
Sp. Gr. of Ohio oil	0.7445	0.7941	0.8245	0.8455	0.9070		0.913

It is peculiar that in distillation under atmospheric pressure as well as *in vacuo* the lowest fraction from the Canadian oil is heavier than that from Ohio oil, while the next following distillates are reversed in the order of their specific gravity. Under the influence of vacuum distillation a large portion of the heavier constituents of the residue above 350°, under atmospheric pressure, are reduced in boiling points to such an extent that the specific gravity of the lower fractions is very considerably increased. Referring to the specific gravity of the fractions from the Apscheron oil, page 48, it will be seen that the corresponding fractions *in vacuo* from the Canadian oil are much heavier, and the residue is much smaller. The differences between the weights collected at different temperatures in the Canadian and Ohio petroleum also confirm the marked variation in composition already referred to, and an explanation must evidently be sought in the larger quantities of the series C_2H_{2n+2} in the fractions below 150° from Ohio oil, and the greater quantity of the heavier oils of the series C_nH_{2n} and similar series in distillates from Canadian oil above this point.

The percentages of sulphur in these distillates were also determined:

	–100°	100°–150°	150°–200°	200°–250°	250°–300°	300°–350°	Residue.
Sulphur	0.25	0.45	0.47	0.75	0.78	0.81	0.83

When distilled without much decomposition the sulphur compounds in Canadian oil collect in smaller quantities in the lower distillates than is the case in Ohio oil.

Determinations were made of the per cent of bromine absorbed by the vacuum distillates: —

	100°	100°–150°	150°–200°	200°–250°	250°–300°	300°–350°	Residue.
Bromine abs.	0	3.25	4.59	6.2	8.2	15.8	25.82
Bromine abs. atm. pressure		0.67	1.12	3.49	8.39	14.4	17.8
Br. abs. Ohio oil, vac. dist.	0	4.57	6.60	250°–350° 7.08			24.38

There is a marked difference in bromine absorption between the distillates collected *in vacuo* and those collected under atmospheric pressure. The capacity for absorbing bromine in the distillates from Canadian oil is greatly increased in the lower fractions by vacuum distillation, and this difference is even more noticeable in Ohio oil. It is probably due to the smaller amounts of Canadian oil distilling at lower temperatures under atmospheric pressure. The larger quanti-

ties of bromine absorbed in the fractions collected *in vacuo* is suggestive. It cannot be caused by decomposition, but it seems to be due rather to the reduction in boiling points by which certain compounds capable of absorbing bromine are carried over at lower temperatures, and doubtless too with less decomposition. The increased absorption above 250° may indicate cracking, or the presence of normal constituents that absorb bromine. Since the difference in the amounts absorbed in the Canadian oil *in vacuo* and under atmospheric pressure is not large except in the residues, and the conditions much less favorable for cracking in the vacuum distillates, it would seem that the absorptive capacity is due to normal constituents of the crude oil.

The fraction 150°–200°, containing 0.47 per cent of sulphur, absorbed 4.59 per cent of bromine. A portion was treated with alcoholic mercuric chloride, washed, dried, and it was then found to contain 0.063 per cent of sulphur. A determination of the amount of bromine it absorbed gave 2.8 per cent. This result is evidently independent of the sulphur compounds. It must indicate either normal constituents of the oil with an affinity for bromine, or the presence of decomposition products due to cracking.

Another portion of the same fraction was agitated with concentrated sulphuric acid, and the quantity of bromine then absorbed was equivalent to 1.15. Since mercuric chloride has been shown to remove nearly all the sulphur compounds from the lower fractions, and sulphuric acid only partially, it is still further evident that there are present in this fraction other bodies capable of absorbing bromine, perhaps unsaturated hydrocarbons, either contained in the crude oil or resulting from decomposition during distillation.

The distillates collected *in vacuo* showed but slight indications of decomposition; they were only slightly discolored, except the residue above 350°. In prolonged distillation the higher fractions gradually become colored by polymerization or other decomposition. Even the residue above 350° showed scarcely any odor, and it had apparently undergone but little decomposition. The distillates above 150° and the residue above 350° are reserved for further study.

As in the study of Ohio petroleum, the lower members of the series C_nH_{2n+2} were sought for in the most volatile refinery distillate. Twenty litres of the very first distillate from Petrolia crude oil was submitted to distillation, and the vapors collected in a Warren condenser filled with a freezing mixture or with water, according to the boiling points of the distillates, and with a condensing worm in front filled with the freezing mixture. Distillates were collected below 45°, and the dis-

tillation of them repeated until they collected for the most part within well defined limits. The following weights were collected as representing the quantities of these products in the twenty litres first distilled: —

—10°	10°–20°	20°–25°	28°–30°	30°–35°	36°–38°
100	40	30	175	30	80

The small quantities distilling at temperatures outside of the boiling points of the well known hydrocarbons were not further examined, since it was assumed that they were merely mixtures. The portion collecting at 29°–30° in a vapor density determination gave 2.54; required for is opentane 2.49.

A vapor density determination of the fraction 36°–37° gave 2.66, which corresponds to the composition of pentane, C_5H_{12}.

Distillation of the portion —10° was continued until 20 grams collected between 7° and 8°. In a vapor density determination by the method of Hofmann, the value 2.01 was obtained; calculated for butane, C_4H_{10}, 2.01. A considerable portion of this oil collected below 5°; which consisted chiefly doubtless of the butane that boils at 0°. But since this body has been identified no further attempts were made to separate it more completely. Concerning the butane boiling at 8°, what has been said of the same product separated from Ohio petroleum applies also here. It is evident from the weights collected of these volatile hydrocarbons that they are present in much smaller quantities than in Ohio petroleum.

The distillate below 150° *in vacuo* was fractioned twelve times, collecting at first within 5° limits, then within 2°, and finally within 1°, with the aid of Warren condensers containing glass coils and Hempel columns. At the end of the eighth distillation, the last seven under atmospheric pressure, the lower distillates collected as follows, with smaller quantities between these limits: —

	—55°	55°–60°	65°–69°	77°–83°
Grams	8	25	40	65

As was mentioned when considering the lower fractions of the Ohio oil, these weights evidently represent only approximately the quantities in the crude oil.

After the eighth distillation, the fractions 55°–60° were further purified, until 15 grams distilled constant at 60°–61°, bar. 749 mm., and a vapor density determination of this product gave 2.96; required for isohexane, 2.98.

At 67°–68°, after the twelfth distillation, 10 grams of oil collected, which gave as its vapor density 3.01; required for hexane, 2.98. The distillates 75°–85° will be considered with the aromatic series.

At 87°–93°, after the eighth distillation, the distillates amounted to 115 grams, and after the fifteenth, 20 grams distilled at 90°–91°, bar. 745 mm. A vapor density determination of this product gave 3.51; isoheptane, C_7H_{14}, requires 3.46.

At the end of the seventeenth distillation, 80 grams collected at 96°.5 – 97°.5, bar. 740 mm., which distilled constant within these limits. A determination of its vapor density gave 3.63; required for heptane, 3.46. The composition of this oil was further established by analysis: —

0.1870 gram of the oil gave 0.5781 gram CO_2, and 0.2514 gram H_2O.

	Required for C_7H_{16}.	Found.
C	84.00	84.31
H	16.00	15.77

Outside of the limits of temperature within which the hydrocarbons C_nH_{2n+2} have been found, the distillates below 105° have been subjected to prolonged distillation, but the quantities collected were so irregular, gradually separating into higher and lower constituents, that it excluded the presence in any considerable quantity of other bodies. The fractions in the vicinity of 111° will be described later, in the examination for toluol.

Concerning the distillates collected at 118°–119°, the observations on the corresponding fractions from Ohio oil apply equally here. At 118°–119°.5, the distillates amounted to 90 grams after the fifteenth distillation. A vapor density determination gave 4.02; required for octane, C_8H_{16}, 3.94. As in the case of the Ohio products, this fraction was purified with much care, and the following determinations of carbon and hydrogen were made: —

I. 0.2013 gram of the oil gave 0.6226 gram CO_2 and 0.2738 gram H_2O.

II. 0.2036 gram of the oil gave 0.6318 gram CO_2 and 0.2799 gram H_2O.

III. 0.2045 gram of the oil gave 0.6324 gram CO_2 and 0.2762 gram H_2O.

	Required for C_8H_{18}.	Found. I.	II.	III.
C	84.20	84.35	84.61	84.33
H	15.79	15.12	15.28	15.01

From the low percentage of hydrogen and higher percentage of carbon it was evident that this oil still contained a small amount of a hydrocarbon with less hydrogen, probably of the series C_nH_{2n}, although the main constituent was evidently a member of the series C_nH_{2n+2}. In further attempts to eliminate the hydrocarbon with less hydrogen, the remainder of the oil after analysis was treated several times with hot nitric and sulphuric acids, and boiled repeatedly with sodium until there was no residue left on distillation. Although the boiling point was not materially changed by this treatment, analysis showed a decrease in the percentage of carbon to 83.91 per cent, and an increase in hydrogen to 16.10 per cent.

As in the Ohio oil, we found that distillates collected with much persistence between 120°–126°; after the eleventh distillation, the following weights were obtained: —

	120°–121°	121°–122°	122°–123°	123°–124°	124°–125°	125°–126°	126°–127°	127°–128°
Grams	85	70	80	60	30	30	70	60

The quantities between 122°–125° were not greatly diminished after the sixteenth distillation; and, like the distillates from the Ohio oil, these products contained small quantities of the aromatic compounds; they will receive further attention with reference to their chemical reactions. After the twelfth distillation, 110 grams of an oil collected at 126°–128°, bar. 752 mm., which was carefully purified in the manner already described. It gave, by the method of Victor Meyer, a vapor density corresponding to octane, C_8H_{18}; found, 4.24; required, 3.95. What has been said concerning the presence of the octanes in Ohio petroleum applies also to these distillates from Canadian oil, and they evidently require further study. The fractions collected at 130°–142° will be considered with the aromatic series. A distillate persisted at 145°–146°, as shown by the quantities collected at the twentieth distillation: —

	142°–143°	143°–144°	144°–145°	145°–146°	146°–147°	147°–148°
Grams	30	32	50	75	25	22

Since the fractions 144°–146° resisted all attempts to separate them into bodies with higher and lower boiling points, further study is necessary to determine whether they represent an individual product.

Between 149°–152°, 160 grams collected at the tenth distillation, a large portion of which distilled constant at 150°–151°, bar. 749 mm. After treatment with nitric acid and sodium, with results similar to those observed in the Ohio oil, this product gave, in a vapor density

determination, a value required for nonane; found, 4.56; required for C_9H_{20}, 4.43. Distillation of the fractions from Canadian petroleum above 160° cannot be continued under atmospheric pressure without decomposition, probably caused by the action of air upon the hot oil. Unless, indeed, as some attempts have shown, it will be possible to distil them in an atmosphere of carbonic dioxide. These fractions have been distilled several times *in vacuo*, and further study of them is reserved.

From the results thus far obtained, it seems that the series C_nH_{2n+2} is represented in Canadian oil by the same members as are found in Ohio and Pennsylvania oils, but the lower hydrocarbons are present in much smaller proportions. The peculiar properties of Canadian oil depend, at least partially, on the small quantities it contains of the hydrocarbons C_nH_{2n+2}. The sulphur compounds exert an important influence. The presence of unsaturated hydrocarbons is not yet determined. Whether other series of bodies characterized by their instability form important constituents of the oil can only be ascertained by a critical study of the portions with high boiling points.

Aromatic Hydrocarbons.

Series C_nH_{2n-6}.

Benzol.

In looking for members of the aromatic series, the same methods were followed as in fractions of the Ohio oil. At the end of the eighth distillation, 20 grams collected at 77°–79°, 15 grams at 79°–81°, and 30 grams at 81°–83°. In treating these fractions, which contain benzol, with nitric acid under the conditions necessary for the formation of nitrobenzol, avoiding loss, so far as possible, and distilling off the unaffected hydrocarbons, the first fraction gave 2.8 per cent of benzol, the second 4.4 per cent, and the third 4.14 per cent. The benzol calculated from these data, in the total weight of the fractions, gave three grams as the total weight in the 64.5 kilos of crude oil taken, equivalent to 0.0047 per cent. Practically all the benzol was collected within these limits, since scarcely any nitro product was obtained in the higher and lower fractions. The quantity of benzol in the crude oil is probably somewhat larger than is here represented, although it must be considered as somewhat less than the amount contained in Ohio oil. Some loss undoubtedly resulted from distillation *in vacuo*, as well as in the subsequent separations. The

nitrobenzol was recognized by conversion into aniline, which gave its characteristic reaction with furfurol.

Toluol.

In the portions containing toluol, between 107°–109° after the eighth distillation, the distillates amounted to 40 grams, at 109°–111° to 250 grams, and at 111°–113° to 50 grams. These fractions were treated for the formation of nitrotoluol in the same manner as those previously examined, and the fraction 109°–111° gave a weight of unaffected hydrocarbon and nitro product equivalent to five per cent of toluol in the fraction 107°–109° one per cent, and in the fraction 111°–113° one per cent. The higher and lower fractions gave no nitrotoluol. Referred to the total weights of the fractions, the quantity of toluol was 3.4 grams, equivalent to 0.005 per cent of the total weight of crude oil taken. As in the case of benzol, it is probable that the quantity of toluol is somewhat larger than is shown by these determinations. This product was shown to be toluol by conversion of the nitro derivative into toluidine, which gave characteristic color reactions.

Xylols.

The single allusion to the presence of xylols in Canadian petroleum is a general statement by Schorlemmer that he obtained reactions for benzol and its homologues, although the only aromatic hydrocarbon he separated was cumol in the form of the trinitro derivative.

After prolonged distillation, having found that fractions collected within limits corresponding to the boiling points of the xylols, we have spent considerable time in the formation of characteristic compounds as adequate evidence of their presence in the crude oil. In the twentieth distillation, within one degree after the twelfth, the following weights collected between 136° and 143°: —

	136°–137°	137°–138°	138°–139°	139°–140°	140°–141°	141°–142°	142°–143°
Grams	30	40	25	40	25	47	30

On account of the close proximity of the xylols in boiling points, it would evidently require much longer time in distillation and larger quantities of the distillates to separate them completely. We therefore depended upon the formation of derivatives that are sufficiently well characterized to warrant conclusions concerning the xylols from which they were formed. As a qualitative test for paraxylol, a part of the fraction 137°–138° was heated with nitric and sulphuric acids,

and the oil which separated was allowed to stand until a crystalline product formed. After crystallization from alcohol, the nitro derivative thus obtained melted at 139°–140°, the melting point of trinitroparaxylol. Another portion of the same fraction was boiled during several hours with chromic acid, and the solution extracted with ether. Upon evaporation, a white powder remained that sublimed without melting, and resembled in its appearance terephthalic acid. To determine the quantity of paraxylol according to the method suggested by Levinstein, a measured portion of the fraction 137°–138° was shaken during thirty minutes with concentrated sulphuric acid. The loss in volume corresponded to 10.77 per cent, representing the other aromatic hydrocarbons. The residual oil was then agitated with fuming sulphuric acid to dissolve the paraxylol, with a diminution in volume representing 9.02 per cent of the xylol.

The quantity of metaxylol in fraction 139°–140° was found by treating it first with dilute nitric acid, which, according to Brückner,* should not affect metaxylol, and distilling with steam, which carries over the metaxylol. The loss in volume, 7.5 per cent, was noted, and the distillate was agitated first with ammonia, then with concentrated sulphuric acid; the last diminution represented 8.8 per cent of metaxylol.

Many attempts were made to prove the presence of orthoxylol by the formation of the nitro compounds, and toluic acid. But no di- or tri-nitro compounds could be separated after treatment with nitric acid except those whose melting points corresponded to metaxylol. By the action of dilute nitric acid, which should not affect metaxylol, an acid was formed, but not in sufficient quantity to show that it was toluic acid. In forming the sulphonic acids and the sodium salts, so far as could be observed, no sodium orthoxylolsulphonate was present. It is quite possible that orthoxylol could be detected in a larger quantity of product. The larger amounts of the fractions 140°–142° therefore consisted partially of metaxylol. Referring the quantities of meta- and para-xylol to the weights of crude oil, the amount of paraxylol is 0.006 per cent, of metaxylol 0.003 per cent, in their respective fractions. These numbers cannot be assumed to represent more than an approximate estimation of these xylols, although they are doubtless, for the most part, collected in the fractions 137°–143°. In fractions 141°–143° the amount of sodic xylolsulphonate formed corresponded to 0.009 per cent of xylol, and, since orthoxylol could

* Ber. der deutsch. chem. Gesellsch., 1876, p. 405.

not be detected, this quantity should be added to the total amount of metaxylol in the crude oil. Even then 0.012 per cent is scarcely more than a trace of this body. As in the similar determinations in Ohio oil, these results serve to show the very small proportion of the xylols contained in the crude oils. In the distillates 130°–140° of the Canadian oil there were indications of bodies capable of forming nitro products, but much larger quantities of these fractions will be needed for their separation.

Series C_nH_{2n}.

The fraction 68°-69° of the twelfth distillation was carefully purified with alcoholic mercuric chloride, nitric acid, sulphuric acid, and distillation with sodium. A combustion then gave the following results: —

0.1889 gram of the oil gave 0.5784 gram CO_2 and 0.2719 gram H_2O.

	Required for C_6H_{14}	Required for C_6H_{12}	Found.
C	83.71	85.71	83.45
H	16.28	14.28	15.99

This fraction therefore consisted essentially of hexane, and it contained no appreciable quantity of hexahydrobenzol.

The fraction 97°–98°, by the action of a mixture of nitric and sulphuric acids, gave a nitro compound heavier than water, equivalent to 10 per cent of the weight taken. The heavy oil turned red with sodic hydrate, and partially dissolved, reprecipitating with acids. By reduction with tin and hydrochloric acid, a substance with the properties of an amido compound was formed. It distilled with steam, was soluble in acids, and was precipitated from the acid solution by sodic hydrate. The prolonged fractional separation excluded benzol, and furthermore the amido derivative gave no reaction with furfurol. In its behavior toward sodic hydrate the nitro compound resembled the unsaturated nitro compounds of the series C_nH_{2n}, but the quantity of the distillate was not sufficient for complete verification. Another portion of the same fraction was heated during several hours with dilute nitric acid, the solution neutralized with sodic hydrate, and evaporated to dryness. A portion dissolved in water gave, with ferric chloride, the characteristic color for acetic acid, and more of the sodium salt, decomposed with hydrochloric acid and extracted with ether, gave colorless prismatic crystals resembling succinic acid.

In a distillate 95°–100°, from the Caucasus petroleum, Beilstein and

Kurbatoff * observed the formation of acetic acid, considerable succinic acid, and other non-volatile acids. The oil remaining after the treatment with nitric acid, was distilled with sodium, and a combustion gave the following results already stated on page 56 : —

	Required for C_7H_{16}.	Required for C_7H_{14}.	Found.
C	84.00	85.71	84.31
H	16.00	14.28	15.77

Since hexahydrotoluol is not affected by nitric acid, but is completely decomposed by a mixture of nitric and sulphuric acids, it cannot be present in any appreciable quantity in this fraction.

In examining the fraction 118°–119° for hexahydroisoxylol, after the sixteenth distillation it was heated with a mixture of nitric and sulphuric acids. The acid was much colored from decomposition, and crystals separated which were very sparingly soluble in alcohol. The purified substance melted at 178°, the melting point of trinitroisoxylol. Hexahydroisoxylol was therefore present, although it formed but a small part of this distillate, as shown by the results of combustions repeated from page 56. It should be borne in mind that the oil analyzed was purified with nitric and sulphuric acids separately : —

	Required for C_8H_{18}.	Required for C_8H_{16}.	Found. I.	Found. II.	Found. III.
C	84.20	85.71	84.35	84.61	84.33
H	15.79	14.28	15.12	15.28	15.01

By further treatment with the acid mixture the hexahydro compound was sufficiently removed to prove the presence of a hydrocarbon C_nH_{2n+2}, as shown by the results of analysis already given.

With the limited quantity of distillates 136°–138°, which should contain hexahydromesitylene if it is a constituent of Canadian petroleum, remaining from the examination of the xylols, satisfactory conclusions could not be reached concerning the presence of this hydrocarbon. Since Markownikoff has recognized it in the Russian oil, it is very possibly present in the Canada oil. As in the Ohio fractions, after removing the xylols by continued action of the acid mixture, we obtained a small quantity of an oily nitro product that did not crystallize. With a larger supply of this distillate, further attempts will be made.

The lines of study which are now in progress on the Ohio and

* Ber. der deutsch. chem. Gesellsch., 1880, p. 1820.

Canadian oils have been indicated in the preceding pages. Besides the higher vacuum distillates sodium salts of acids have been separated whose composition is now being determined. The facts thus far accumulated are not sufficient to determine whether the acids exist as such in the oils, as is maintained by Aschan, or whether they are oxidation products of other constituents, as Engler and Lachowitz believe. Since sodium salts have been obtained which contain much nitrogen and give the characteristic odor of pyridine compounds when heated, the possibility of pyridine carboxylic acids is suggested. In searching for the oxygen and nitrogen compounds we have separated bodies that give with nitric acid a brilliant red color, similar to what was early observed in our study of the sulphur derivatives.

The characteristic qualities of Canadian petroleum which appear in the results of this examination may be summarized as follows: —

1. In its high specific gravity and in the proportions that distil at different temperatures, Canadian petroleum approaches the Russian oil more nearly than the Ohio petroleum. But the specific gravity of the distillates is lower, approaching those of Ohio oil. As indicated by its lower specific gravity, Oil Springs oil is essentially different from Petrolia oil. This is especially evident in the lower percentage of sulphur, the larger quantities of the distillates, the higher specific gravity of these distillates, and the higher bromine absorption.

2. Petrolia oil is composed principally below 150° of members of the series C_nH_{2n+2}, although in much smaller quantities even than in Ohio oil. Another series is present capable of forming nitro products resembling the nitro compounds of the series C_nH_{2n+2}, or the unsaturated hydrocarbons C_nH_{2n}.

3. The aromatic hydrocarbons C_nH_{2n-6}, benzol, toluol, para- and meta-xylol are present in minute proportions. The hexahydro series is represented by hexahydroisoxylol, and probably by higher members.

4. By the behavior of the distillates toward bromine, the presence of hydrocarbons capable of forming addition products is indicated, as well as the formation of unsaturated hydrocarbons due to cracking in the distillates above 200° or 250°.

5. As in Ohio oil, the sulphur compounds have a tendency to collect in the higher fractions.

In the prosecution of this work I have received valuable aid from my assistants, Messrs. Cleveland, Little, and Giessen, and in portions of the work on the Canadian petroleum, from Mr. W. H. King, a student in this Laboratory.

Origin of Petroleum.

In the clear and concise statement of the present condition of the theoretical discussion concerning the formation of petroleum by Professor Edward Orton (Geological Survey of Ohio, 1890), without including the thory of Mendelejeff that highly heated iron or iron carbides within the earth may furnish the world's supply, it is explained that most geologists accept the view that organic matter of vegetable or animal origin constitutes the source, and that it was deposited during the formation of the rock strata. Many insist on substances of vegetable origin as the chief source, and depend upon destructive distillation as an essential agency. A small minority of the geologists, and some chemists, especially the Germans, hold that animal remains may be accepted as the sole source in a process of primary decomposition without distillation.

The chief difficulty in arriving at any satisfactory conclusion concerning the formation of petroleum depends upon the fact that the principal process is completed, and there remains scarcely a trace of the stages through which the original substances have passed; or indeed these stages may have been so simple that we have before us in the oil rock all the indications that could ever have been observed concerning the formation of petroleum. Prevailing opinions seem to refer the genesis of the limestone oils to the decomposition of animal remains, and that of other oils to vegetable decomposition.

The most interesting observation on the natural formation of oil that has come to my knowledge is the experience of Mr. R. A. Townsend, of Petrolia, who has recently returned from India, where during fourteen years he has been engaged by the British government in prospecting for minerals and oils. In the oil region of Assam, Beloochistan, and the Punjaub, the surface is bare rock, and the anticlinals are easily located. Approaching an elevation while prospecting, he found at the top a bell-shaped depression, into which he descended to a vertical depth of 2,000 feet, and came upon beds of Tertiary oysters from which petroleum was exuding. The excavation had been formed by a thermal spring that had disappeared, leaving the strata bare. No oil was observed above or below the oyster beds. In oil territory owned by Mr. Townsend in Assam, half decayed tree trunks greasy with oil have been excavated.

One of the serious difficulties for those who believe in destructive distillation is an adequate source of heat. Organic matter, animal or vegetable, decomposes readily enough when exposed to the air at ordinary temperatures, but the products are very different from petroleum.

In the early development of organic chemistry, the nature of the products resulting from the destructive distillation of various forms of organic matter was recognized. Dippel's oil distilled from bones contains the nitrogen compounds pyrrol, pyridine, and their derivatives. Reichenbach (Schweigger's Journal, LXI. 273) identified paraffine as one of the distillation products of animal and vegetable bodies.

As already mentioned, Warren and Storer established the presence of the hydrocarbons C_nH_{2n+2}, C_nH_{2n}, and C_nH_{2n-6} as distillation products of a lime soap prepared from menhaden oil. More recently Engler has also prepared the petroleum hydrocarbons by the distillation of menhaden oil under pressure. There can therefore be no question as to the ready formation of petroleum from animal bodies when decomposed with the agency of heat. But that the same

products may be formed without the aid of high temperatures is not so easily demonstrated. That any considerable elevation in temperature has accompanied the formation of petroleum, at least in the limestones, is rendered extremely improbable by the condition of the oil rock. Sections of the Corniferous limestone from wells drilled at Petrolia exhibit very plainly the conditions of stratification, without the slightest indication of metamorphic action. The rock consists of alternate light and dark layers, the light portion being much more compact than the darker strata, which are more granular, and offer greater resistance to the drill. As our analyses show, the two varieties of rock do not differ essentially in their composition. The darker portions of the strata evidently contain more oil.

Concerning the question as to whether petroleums can be sharply divided as to their origin, the limestone oils having their source in the decomposition of organic matter of animal origin, and other petroleums in the decomposition of vegetable matter, more experimental evidence is necessary.

The absence of nitrogenous organic bodies in petroleum has been suggested, by the adherents of vegetable matter as the source, as a serious objection to its origin in the decomposition of animal bodies. It is true that in other oils than those found in the limestones the quantities of nitrogen hitherto found are extremely small, as already explained (page 16). As further evidence of the minute proportion of nitrogen in non-sulphur oils, we have determined this element in Chinese petroleum (1), in a colorless Italian petroleum (2), in Macksburg, Ohio, oil, 1,900 foot level (3), and in a peculiar light yellow Berea Grit oil, 500 foot level (4), from Archer's Fork, Ohio, that is at present refined in large quantities. The last named oil deposits paraffine when cooled to 10°.

Determinations by the Kjeldahl method gave the following results: —

	Trenton Limestone Oil.	Corniferous Limestone Oils.
(1) 0.10	(1) 0.26	(1) 0.16
(2) 0.014	(2) 0.23	(2) 0.18
(3) 0.035	(3) 0.21	(3) 0.21
(4) 0.023	(4) 0.13	
	(5) 0.35	
	(6) 0.08	
	(7) 0.07	
	(8) 0.05	
	(9) 0.05	
	(10) 0.16	
	(11) 0.05	
	(12) 0.06	

It is therefore evident that in general a higher percentage of nitrogen is a distinctive quality of the limestone petroleums.

As mentioned above, we now have in hand certain nitrogenous bodies extracted from Ohio petroleum which resemble derivatives of the pyridine bases. In our earlier work on the sulphur compounds in the limestone oils (These Proceedings, XXV. 228), there were indications that these petroleums contain certain ethereal oils of vegetable origin beside other oils resembling the terpenes. A question may therefore arise as to whether the limestone oils have been derived exclusively from organic matter of animal origin.

Recently Zaloziecki (Ber. der deutsch. chem. Gesellsch., 1894, p. 2081) has separated from the sulphuric acid extract of Galician oil, bodies which he concludes indicate the presence in the crude oil of the terpenes or allied substances.

On chemical grounds it seems reasonable that changes in organic bodies during long periods of time with exclusion of air, under enormous pressure, are sufficient to explain the formation of petroleum. The modifications that have been observed in various forms of chemical reactions under high pressure would seem to indicate that organic bodies should be affected quite differently than under ordinary conditions. I have in view some experiments on the behavior of organic matter under continued high pressure, fifty to one hundred tons per square inch, for the purpose of ascertaining what changes, if any, may result.